MUNICIPAL SCHOOL OF TECHNOLOGY, MANCHESTER.

The Municipal School of Technology

SACKVILLE STREET, MANCHESTER

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PRINCIPAL - J. H. REYNOLDS, M.Sc.

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The Municipal School of Technology has for its chief object the due training of suitably prepared students in the application of science to industrial pursuits, especially to those industries which are of chief importance to the commercial well-being of South-East Lancashire, namely : Mechanical, Electrical, and Sanitary Engineering; Applied Chemistry, including Bleaching, Dyeing and Printing, Paper Making Manufactures, Brewing and Metallurgy; Spinning and Weaving of Cotton and Mixed Fabrics. Courses in collaboration with the University and the School of Art are also offered in Architecture.

Students who have passed the Examinations of the Joint Matriculation Board of the Northern Universities or other qualifying Examination may proceed after a three years' course to the Degree of Bachelor of Technical Science (B.Sc. Tech.) of the University of Manchester, and subsequently to more advanced degrees, whilst provision is also made for the award of Certificates of the University in the before-named and other subjects of study.

The School is exceptionally well equipped with extensive laboratories with appliances for scientific and technical study, and opportunities for special study in research are also accorded. Facilities are afforded, where they are desired, to properly qualified students for the study of special subjects in any course.

The instruction is given by means of lectures and tutorial exercises, accompanied by suitable work in the laboratories and workshops, and by visits of inspection to well-equipped industrial concerns and to public works.

The tuition fees are £21 per annum. In addition there are charges for registration, books, appliances, etc., amounting to about £6 per annum.

For fuller particulars of the courses the School Calendar should be consulted, price by post, 10d.

THE JOURNAL OF THE MUNICIPAL SCHOOL OF TECHNOLOGY

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OF

THE MUNICIPAL SCHOOL OF TECHNOLOGY, MANCHESTER

A RECORD OF INVESTIGATIONS
UNDERTAKEN BY MEMBERS
OF THE TEACHING STAFF OF
THE SEVERAL DEPARTMENTS
OF THE SCHOOL

MCMVIII.

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PREFACE.

THE new and important building known as the Manchester Municipal School of Technology, erected by the Corporation of the City in Sackville Street, was begun in 1895, and was opened for the purposes of instruction in October, 1902, by the Prime Minister, the Right Hon. A. J. Balfour, M.P. In the course of his address he referred to the School in the following terms :—

> "This building is perhaps the greatest fruit of its kind, the greatest fruit of this kind of municipal enterprise in this country. . . . Nobody can go over this building, observe its equipment, study even in the most cursory manner the care which has been devoted to it, without feeling that the Corporation of this great City have set an example worthy of the place they hold in Lancashire, worthy of the place they hold in Great Britain."

The exceptional opportunities which the unique equipment of the School has placed at the command of the professors has enabled them, with the co-operation of other members of the staff, and occasionally with the assistance of the more advanced students, to enter, as opportunity serves, upon original investigations of scientific and technical interest. Many of these have been communicated to scientific and technical journals, and to various professional associations, and have met with much acceptance.

With a view to make known the important work of the School in this regard, and to give the opportunity for the exchange of the results of original investigations conducted in other institutions, the Committee of the School has sanctioned the production at the School Press of a selection, prepared by a Committee of the Board of Studies, of the more valuable of these investigations, and now issue them to the public under the title of "The Journal of the Municipal School of Technology, Manchester."

It is proposed to arrange for the issue at short intervals of succeeding numbers of the Journal, and it is hoped that the publication of these memoirs may serve to show that not only is the staff sedulously engaged in the serious and important business of technical training and instruction, but that a no less serious attempt is being made to widen the bounds of knowledge, not only in pure science but in its application to industrial needs.

The Equipment of the Mechanical Engineering Laboratory of the Municipal School of Technology

By Prof. J. T. NICOLSON, D. Sc., M. Inst. C.E.

IN the course of a tour of inspection of the American and Canadian Technical Colleges & Engineering Schools in the year 1897, made by Mr. (now Principal) J. H. Reynolds, as Director of Technical Instruction of the City of Manchester, the author's laboratories at McGill University, Montreal, were visited, and the question of the type of an experimental engine for the new Technical School, then in course of erection in Manchester, came under discussion. An arrangement was subsequently made whereby designs for this engine were prepared under the supervision of the author, when in Britain during the summer of 1898; and this finally led to his being offered an appointment by the Manchester Technical Instruction Committee to take charge of the equipment of the Engineering Department of the new School. As this equipment gave promise of being upon a scale never before attempted in Europe, it was with much satisfaction that the author undertook the work and was able to make a serious commencement *in situ* in June, 1899. With unexampled foresight the Committee arranged that the author's whole time should be devoted to this task, and no lecturing or other teaching work was expected from him whilst the design and installation of the laboratory equipment was in progress. A staff of four draughtsmen was placed at his disposal for the carrying out of the work intrusted to him, and it is but seldom that such an opportunity has been afforded for the provision of the best possible experimental plant. In the author's view, the thanks of the engineering profession are due to the Committee and Director of Technical Instruction of this City for the courage and enterprise which they have displayed in taking up and carrying through the equipment of these laboratories, on a scale and with a completeness which is certainly without parallel on this side of the Atlantic at the present time. It is of the first importance, in order to form an opinion as to the appropriateness of the experimental engineering plant installed in the School of Technology to the position it should occupy, and to the needs it is required to supply, that there should be a clear understanding of the guiding principles which underlay the scheme of equipment submitted by the author, and sanctioned by the Technical Instruction Committee. These principles, as enunciated in correspondence with the Director of Technical Instruction in 1899 were as follows :—The laboratory of a high school of engineering

should serve the following purposes in the education of the young engineer :

1. It must help him to understand the principles of the experimental sciences by the use of apparatus embodying those principles in an objective manner.

2. It must enable him to learn the experimental data, and to absorb the fundamental facts, of those sciences by means of machines for testing the properties of the materials used in the mechanical arts, and of instruments for observing and measuring the fundamental physical quantities, such as time, mass, weight, length, speed, temperature, pressure, and the like.

3. It must instruct the more advanced student in the art of proving or testing the more usual types of structures, and the commoner varieties of machines; whether for generating, for transmitting, or for absorbing power; and

4. It must include within its scope the provision of facilities for experimental work by the actual leaders of industry themselves—or by trained deputies appointed by them—on the problems of engineering design which present themselves in their daily practice. In such a laboratory it should be possible for standards of perfection to be instituted to which the specimens of any type and class of machine or instrument may be referred; and for a trained staff to be engaged in the constant endeavour to improve the design, both in principle and in detail, of the products of industrial engineering.

The author is not prepared to maintain that, in the laboratory equipment described in the following pages, the high ideal above set forth has been entirely realised; but at all events an earnest attempt has been made to carry into effect the more prominent of the proposals enunciated, in a concrete form.

For the accommodation of the mechanical engineering department a large proportion of the basement floor of the School was made available. An area of 17,280 square feet, out of a total basement area of 53,300 square feet, contained in six separate rooms or halls, was allotted for laboratory purposes. A further space of 3,000 square feet being reserved for steam boilers, electricity station, and ventilation plant. The general basement plan, Plate A, shows the disposition of the whole.

I.—STEAM ENGINE LABORATORY.

This laboratory is situated next to the electricity station and boiler room, so as to be conveniently supplied with steam either saturated or superheated; and has a floor area of 60ft. by 37ft., or 2,220 square feet. A sub-floor gives a further area of 900 square feet. The

general arrangement, Plate I., shows that the principal object, as to size and interest, in the room is a compound horizontal steam engine, driving against a water-cooled band brake on its fly-wheel, and built entirely for experimental purposes.

Experimental Steam Engine. It is a surprising fact, when one thinks of it, that the very best steam engines waste 85% of the coal they feed upon; notwithstanding the unceasing efforts spent by our predecessors and ourselves for more than 130 years in the endeavour to improve them. It is no doubt well known to you that by the laws of thermodynamics it can be proved that no amount of human ingenuity will ever make a steam engine to waste less than about 40% of the fuel it burns. The physical conditions of this planet have this for their necessary consequence; but there is a large margin available for improvement between these two limits, and our efforts must be unceasingly directed to reducing this margin, and to husbanding the natural sources of energy still left to us, which have been, and are still being, so wastefully employed. The broad principles which govern the direction of the improvement of the steam engine are fairly well understood, as shown by the general adoption of higher steam pressures, and the reversion to the use of superheating which is now taking place; but the writer takes leave to remark that a more particular experimental study of the behaviour of the steam in the engine cylinder has shown that a hitherto but little suspected source of loss plays a more important part than has commonly been supposed. He refers to the leakage which takes place, past the admission and exhaust valves, of steam which either never enters the cylinder at all, or, if it does so, passes through without doing any work. Since the years 1895-96, when certain experiments on cylinder condensation were carried out by Professor H. L. Callendar, and the writer, at McGill University, Montreal, a new method of determining the leakage of valves has been instituted, which appears capable of giving results more closely approximating to those actually occurring than those formerly employed—if, indeed, any method can be said to have been employed at all. The results of many such experiments made upon engines of from 50 to 3,500 H.P., have shown that the loss so occasioned may amount to the equivalent of as much as one whole pound of coal per indicated H.P. per hour; and that the usual loss attributable to this source is probably seldom less than 10% of the whole consumption. If this defect could be obviated, a notable step would be taken towards the elimination of the above mentioned difference between the efficiency now ordinarily attained and that which is theoretically possible. The systematic study of the phenomena and laws of this leakage, and consequently of the means to be adopted for its cure, would form a most proper, and in

the author's opinion, a most profitable subject to be taken up in workshop laboratories set up by our large steam engine builders; but so far as the author's knowledge extends, almost no efforts have been made in this direction, it being almost universally assumed that if a valve is tight when at rest, it will be practically tight when in operation. As an exception the firm of Willans and Robinson may be mentioned; Captain Sankey of that firm having kindly given the author some data obtained by him from a series of experiments on the leakage of piston valves. The 200 H.P. engine in this laboratory has been built for the express purpose of studying the questions of the amount and character of the leakage of steam in the case of valves of various types. The engine is of the horizontal compound side by side type, having cylinders 11½in. and 20in. diameter, with 3ft. stroke. It is provided with two cylinders of each size, either of which may be used as desired. One of the 20in. cylinders has slide valves with Meyer expansion plates, and the other has Corliss valves and gear. Of the two 11½in. cylinders one was made by Gebrüder Sulzer, and fitted with their design of drop valves, and the other has Corliss valves and gear of the same type as for the 20in. Corliss cylinder. Thus a comparative study may be made of the efficiency of different types of valves, e.g., Sulzer versus Corliss or Corliss versus slide valves, and of the effect of size-variation by experiments on the 11½in. and 20in. Corliss cylinders. The pressure may be anything up to 150 lbs. per square inch, and the speed up to 110 revolutions per minute. Each end of each cylinder has separate exhaust pipes, so that the amount of steam taken by them respectively can be found by measurement after condensation in separate surface condensers. The ends, sides and pistons of the cylinders are steam jacketed. The steam, when supplied to any of the cylinders, may alternatively go directly into the steam chests, or may be passed through the jackets before entering them. In the latter case it may or may not pass through a water separator. Steam may alternatively be supplied to the jackets directly from the main steam pipe. The total horse-power indicated may reach 350. The special feature of the engine, as already indicated, is its adaptation for testing the rate of leakage of steam past the admission and exhaust valves. For this purpose in the Corliss cylinder, each valve casing is a separate casting bolted to the cylinder with an intermediate thin plate a, Fig. 1, which may either have an opening through it corresponding to the port area, or may be blank so as to shut off the cylinder from the steam chest. Thus when the valves are operated (from the other engine by the crank shaft) under steam pressure, the amount of steam which leaks past the valve when it is closed can be measured by attaching vessels b for catching the leaking steam, to the valve casing, and

FIG I
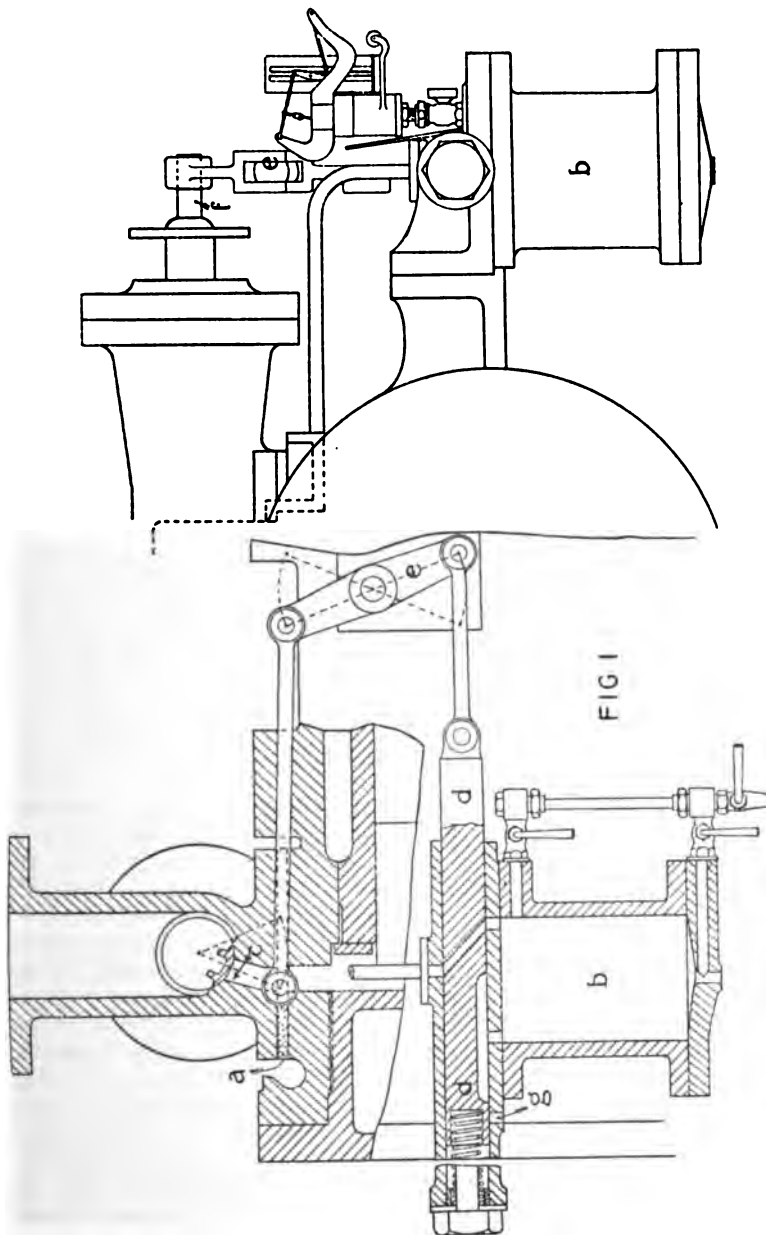
connecting them to the space c between the valve and the blank plate, with the interposition in the connection of a long plug valve d, operated by levers e from the Corliss valve spindle itself f. By preliminarily admitting steam to the vessels b, and then throttling or opening their exhaust pipes g, the conditions of pressure on the two sides of the main valve may be made to approximate to those occurring during actual running, and indicator cards may be taken from the vessels to show the rate of variation of pressure in them, due to leakage, while the valves are in motion. Allowance can also be made for the condensation taking place in the vessels by taking the temperature of their walls and finding the condensation area from these and the cards. In the case of the slide valve cylinder, a thin plate a, Fig 2, is also interposed between the back of the valve-chest face and the cylinder port facings, so that the same experiment can be made with this as with the admission valves of the Corliss cylinders. Recesses have been provided in the back of the valve chest b in which coils of small piping c are placed, so that when desired the valve faces may be heated by circulating steam, or cooled by circulating cold water therein. By this means and by the insertion of thermometers within its substance the valve face may be brought to the same state as to temperature as when working normally. In the case of the Sulzer cylinder, the leak may be studied by cutting off a portion of the cylinder close to each end, from which cards may be taken when the valves are being operated under pressure. In all the four cylinders duplicate exhaust valves of the drop pattern are fitted at each end, Fig. 3. These auxiliary valves a are driven by special gear b from the valve motion, and are arranged to open and close simultaneously with the main exhaust valves, whether of the Corliss, slide valve, or Sulzer pattern. By then taking indicator cards from the spaces c between the main and auxiliary exhaust valves (and by determining the rate of leakage past the auxiliary valves by special experiments), the leakage past the main valves during actual work can be inferred. A very desirable addition to the engine would be a cylinder (say $11\frac{1}{2}$in. diameter and 3ft. stroke) fitted with piston valves so arranged that their rate of steam and water leakage might be studied. When the work already before the mechanical engineering department, in connection with the plant already provided, has been to some extent attended to such an addition will no doubt be seen to be justifiable and desirable. The engine has two surface condensers of differing types; two air pumps of high speed and slow speed designs, and a great number of pieces of accessory apparatus for experimental work. It has been admitted by many competent judges that this engine is a most handsome and creditable production, and one showing that no pains have been spared by Messrs. James
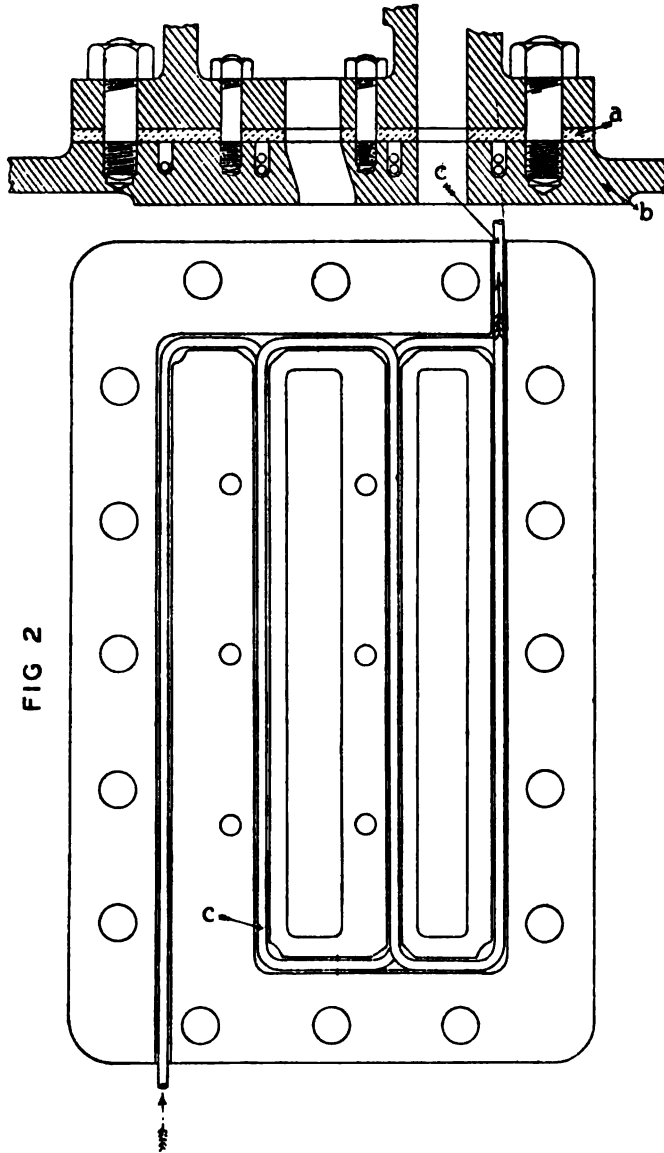
FIG 2

Carmichael and Co., the contracting firm, to complete the work to the full satisfaction of the Technical Instruction Committee and their engineer. In the boiler room there is installed, in addition to the electricity supply and heating service plant, a 500 H.P. steam boiler of the torpedo boat type, J. W. Reed's patent, made by the Palmer's Shipbuilding and Iron Company, Jarrow. It works at 250 lbs. pressure, and serves not only as a reserve boiler for service, but for steam supply to the experimental engines. A superheater of 400 square feet area, Schmidt's patent, manufactured by Messrs. Easton and Co., Erith, is provided for supplying steam of any required degree of superheat to the laboratory.

Automatic Cut-off Simple High Speed Engine. An automatic cut-off steam engine of 50 H.P., by Messrs. The Ball and Wood Engine Co., of Jersey City, U.S.A., is also installed in the steam engine laboratory, and serves for the preliminary drilling of students in the methods of carrying out the details of engine testing. It is fitted with a number of accessories for experimental purposes; including a special indicator reducing gear for high speeds, and a rope brake on the fly-wheel for absorbing the power. A convenient arrangement of hand-wheel and screw on the slack side of the rope, in conjunction with a Horn's tachograph, enables an observer to regulate the speed with great nicety and maintain it at any fixed rate, during a test. The valve faces and the cylinder walls are drilled in several places for the insertion of small mercury thermometers, of the pattern used by the late Mr. Bryan Donkin; and Mr. Mellanby, who had charge of this section of the deparmtent, made elaborate temperature readings in the course of carrying out a number of tests with this engine. This is to constitute a contribution to our knowledge of the way in which the missing quantity is accounted for by cylinder condensation and valve leakage respectively. An interesting piece of apparatus has been fitted in the exhaust pipe of this engine for the direct determination of the amount of wetness of the exhausting steam. The whole of the discharged steam from the engine is dried by causing it to flow over a coil of iron wire heated by the passage of an electric current; and by measuring the quantity of electric energy required to just superheat the steam, the weight of water it contained before passing over the coil can be ascertained. The state of exhaust steam, as to dryness, when it leaves the cylinder of an engine has always been a moot point amongst steam engine theorists, and the author is not aware that the above method of working has ever been resorted to for the elucidation of this important question. Mr. Mellanby's experiments with this apparatus tend to show that the exhaust steam from a simple expansion engine is much drier than might be expected, a fact which goes to confirm the idea that a considerable proportion of

high-pressure steam has leaked across the valve faces directly from steam chest to exhaust passages.

Air Compressor. It is generally supposed that the transmission and distribution of energy by the agency of compressed air is of necessity an extremely wasteful process; and the idea of its ever being able to compete with electricity in this respect has hardly entered anyone's mind. The practical success of the pneumatic system of
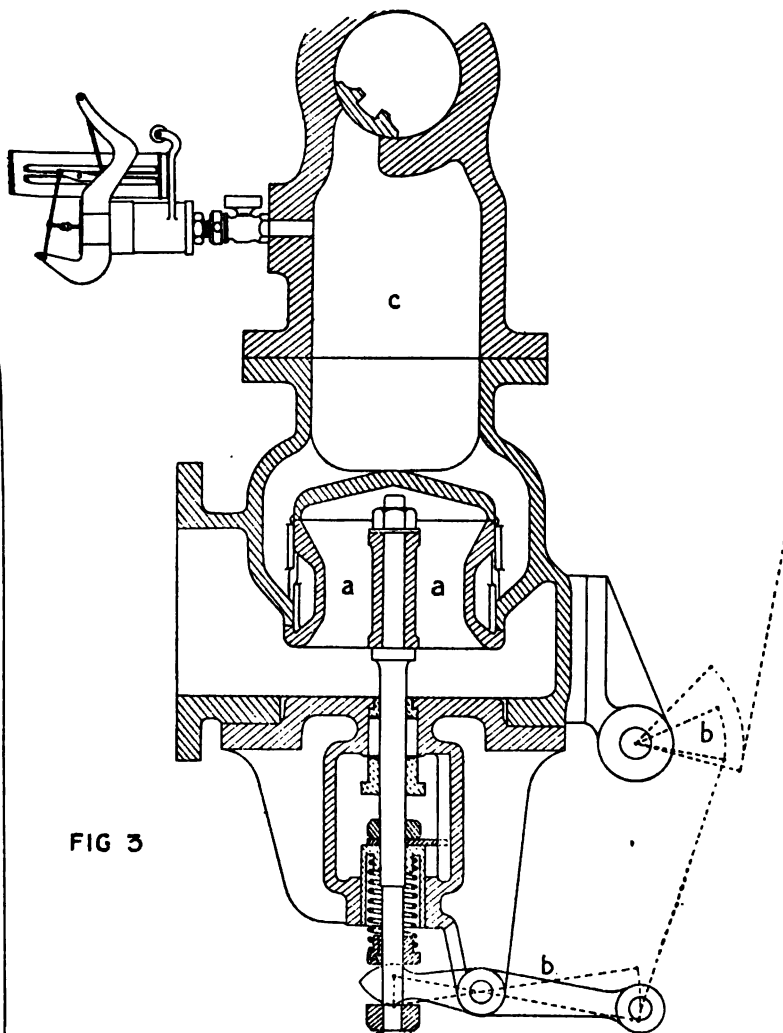
FIG 3

distribution in the City of Paris, where 13,000 horse power are now at work, may be considered to have dispelled this notion. The system there adopted consists essentially of four parts; the air compressor, the air main, the preheater, and the motor. The improvements effected in the mode of compression and in the use of preheated air in the engines have rendered it possible to obtain just as much work at the motor as was supplied at the distant compressors—to obtain, that is, a practical working efficiency of transmission of 100 per cent. This is secured by means of a very insignificant expenditure of coke as fuel in the small stove or pre-heater through which the air passes to the engines. The pneumatic system of power transmission is the only one in which it is possible to insert energy at the working point sufficient to make up for all losses in transmission, without any sacrifice of practical convenience and at an almost insensible cost. The air motors and preheaters in Paris are attended to—or rather left unattended—by waiters and domestic servants who have all manner of other duties to perform. All they have to do is to turn on the stop valve, refill the lubricators, and put on a shovelful of coke once or twice a day. As Professor Riedler (who made an exhaustive report on the Paris system) remarks, "the air motor appears to be an even more long-suffering machine than the steam engine, which is justly renowned in this respect." If the preheater be turned off, the exhausting air may be used for refrigeration. Thus, large confectioners in Paris use their air motors during the day for driving mixing and cutting machines; in the evening they drive their dynamos for lighting, and the exhaust is used for making ice. In summer time, the exhausting of the clean cold air into the workshops is a very great advantage. It would be easy to enlarge on the many advantages of this system of distribution of power; but enough has perhaps been said to show the importance of having an experimental air compressor of the latest type exemplified in the equipment of the engineering laboratories of this School. In compressing air it is of the greatest importance to keep it cool if a high efficiency of the process is desired. If the air could be compressed quite slowly so that the work done upon it by the compressing piston, which is changed into heat (or vibration energy in the particles), had time to pass away into the walls, the compression would take place at the temperature of the entering air (*i.e.*, isothermally) and a notable reduction in the work required to raise the pressure by the desired amount would be effected over what has to be spent if the heat is allowed to accumulate in the air. If, on the other hand, the compressed air is to be used in motors close to the compressor, no great harm is done. When the com-pressing is done so quickly that the temperature of the air rises in the cylinder, then the extra work put in is returned again in the

motors. But if the heated air has to travel through a long main before being used, its temperature has time to fall to that of the ground, and all the extra work necessarily accompanying high temperature compression is thrown away. For transmission purposes, therefore, the most economical way of compressing the air is the isothermal method; and this has long been acted upon in practice by the use of cooling jackets round the cylinder and even in the pistons, as the slow compression process above mentioned would be impracticable, owing to the great first cost of the large machines which would be necessary. For the purposes of a large first-class compressing station, however, this jacket cooling is far from being
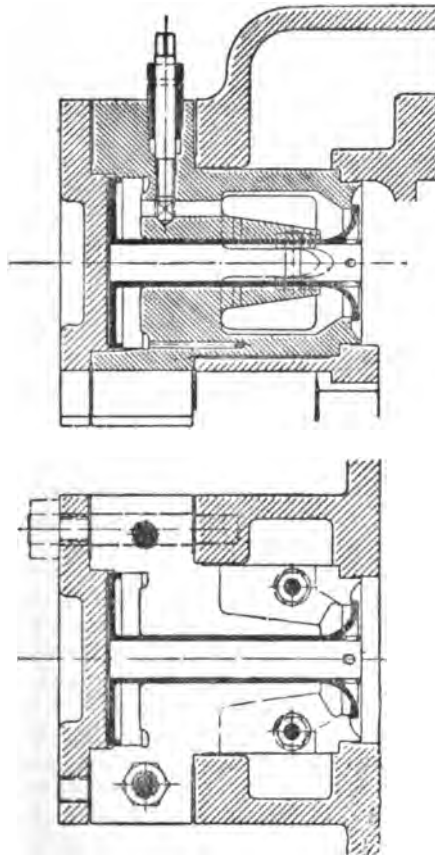
Fig. 4.
Stumpf's Patent Air Compressor Discharge Valve.

the best possible system, and is only to be recommended for mining plants where the injection of a spray of cold water into the cylinder itself is impossible, owing to its impurity or to the undesirability of any additional mechanism. Even with the best forms of spray injection now in use, only a relatively small proportion of the heating can be prevented. Instead of remaining at the temperature of entry, say 60°F., the air, when being compressed to a 100lbs. absolute, heats up to about 300°F., as against 455°F., which would be the terminal temperature if no heat had been taken away at all. A much better method of dealing with the difficulty is to compress in two or more stages. This is accomplished by permitting the air, after its pressure has risen a certain amount, to flow into an intermediate receiver of sufficient capacity to allow of the lowering of the temperature of the air down to that of the atmosphere before it is inhaled into the next cylinder. Professor Riedler applied this method on the 10,000 H.P. installation in Paris with pronounced success. As to the inventor of the plan no certain information is obtainable. The Norwalk Iron Works Co., Conn., constructed compressors on this principle as early as 1881; and Mr. Northcott, of London, made a compound compressor with intercooler as early as 1878. The compressor constructed for the School of Technology is of this two-stage type for pressures up to 150lbs. per square inch. The cylinders are 14in. and 7⅜in. diameter, with 12in. stroke, and are placed side by side. They have water jackets for cooling, but are also furnished with spraying nozzles for injecting water into the cylinders themselves. The comparison between two-stage and single-stage compressions can be carried out by running the large cylinder only, and connecting it direct to the reservoirs. An intercooling receiver is fitted, in which the air, after discharge from the low-pressure cylinder, may be cooled by the further injection of spray; the water being removed by a water interceptor before being admitted to the high-pressure compressing cylinder. The ultimate form of compressor will no doubt be a reversed turbine. Mr. Parsons has already constructed a turbo-compressor to work up to 40lbs. delivery pressure. Meanwhile, the reciprocating compressor holds the field, and in designing an experimental machine of this type the attempt has been made to arrange it so that different types of suction and discharge valve could be fitted at pleasure and their action studied at various speeds and lifts. One set of valves was designed for controlled closure after the manner of Professors Riedler and Stumpf, of Berlin (Fig. 4). They are ordinary mushroom valves made of forged steel, with a central tube acting as guide, and a small piston fitted on its rear end. During compression the air gets behind this piston so that a force is brought to bear upon the valve tending to open it, due to the difference of area of the piston and the

Valve itself. The valve does not open outwards like an ordinary discharge valve; but towards the interior of the cylinder, and in opposition to the air streaming past it when open. The little valve piston also retards the valve, when opening, by acting as an air buffer; the action being regulated by a set screw. The travel of the said piston also limits the amount of valve lift. The valve is closed mechanically by the compressor piston at the end of its delivery stroke. A light spring fitted in the piston pushes it gently to, no matter at how high a speed the compressor may be running. In the Stumpf compressor the inlet valves were cylindrical rocking valves of the Corliss type. The School compressor is driven by a directly connected electric motor, whose speed may be varied between 40 and 300 revolutions per minute by using a water rheostat in the main circuit. The air delivered by the compressor (at any pressure up to 150lbs. per square inch) may be stored in three cylindrical reservoirs, after passing through two smaller ones where it is cleared of cooling water. From these it may be led to the gas and oil engine laboratory, there to be discharged into an air holder from which these engines draw their air. Alternatively, the compressed air may be turned on to a 50 H.P. Ball and Wood high-speed automatic cut-off single cylinder engine for driving purposes. It is the intention, ultimately, to fit a preheater for the air before supplying it to this engine; when the phenomena of this very economical process of transforming heat into work (whereby an additional horse power is obtained for every $\frac{1}{4}$lb. of coke burnt) may be observed and studied. The compressor was built to designs prepared in the School by Messrs. Steven and Struthers, of Glasgow, and reflects credit upon that firm, as a first-class piece of work. For the working out of the design of the valve gear, which required much thought, the author is specially indebted to Mr. P. W. Robson.

2.—THE HYDRAULIC LABORATORY.

General Description. The equipment of the hydraulic laboratory is fairly complete and on a somewhat extensive scale. The elaboration of this department has by some been objected to on the ground that hydraulic power is not made use of to any great extent in this country, and that, therefore, the practical usefulness of such a department would not be great. It may be replied that whilst it is true that we are far behind Continental engineers in experience and skill in hydraulic power utilisation, this is because we have had such an abundance of cheap coal that our water powers have never been exploited. It is certainly not because we do not possess them in abundance. They have not been made available because at present water power is more expensive than steam power. The cost per annum for interest and depreciation upon tne capital expenditure

for the dam, head and tail races, penstocks, gates and wheel-pit of a turbine power plant is from 10s. to £3 per horse power according to the nature of the site of the waterfall impounded. On the other hand, the sum of £4 per annum will amply cover the cost of one horse power obtained from the burning of coal by a large steam engine. The difference between these figures, varying between £3 10s. and £1 per H.P. per annum is what remains available to cover the cost of transforming the power at the water supply into a form suitable for transmission, for its subsequent conveyance to the point where it is to be used, and for its retransformation into mechanical work. The fixed charge and the running expenses of any such transmission have hitherto generally exceeded the above available balance, and the steam engine is found to be the cheaper. But this condition of affairs cannot long continue, even in this favoured country. The day seems to be almost at hand, owing to the great advances which are being made in the means for the transmission of power, especially by the alternate current at high tension, when it will pay to harness waterfalls 50 or 100 miles distant. As coal becomes scarcer hydraulic power will take a more prominent place; and, if the statisticians are correct in saying that in 50 or 100 years coal will cost as much as iron; and that there will be so many people in England that it will be difficult to supply them all with drinking water, the value of water power may be so great that our grandchildren will only be supplied with the precious fluid after it has been depleted of its energy in the shape of mechanical work by passing through turbines! This is, of course, a far-fetched argument in support of a present day hydraulic laboratory equipment; but there are other good reasons to be advanced. Water supply and sewage disposal involve many hydraulic problems, and both these questions are of vital and present interest to us. Great success has attended the distribution of power in our great cities by means of water under high pressure; and this branch of engineering is likely to give employment to many of our young engineers. Hydraulic machinery such as cranes, power-presses, pumps, elevators, etc., occupy a large field in the view of the engineer; and finally the principles of hydraulics, if thoroughly mastered, have a so much more than merely fortuitous analogy to electrical problems, that the study of the one very often facilitates the solutions of the other. The hydraulic equipment in this School is really much more extensive than the space specifically appropriated as hydraulic laboratory would indicate. In addition to the laboratory itself, which is 39ft. by 24½ft., there is a tank house on the roof, with a floor space of 51¾ft. by 10¼ft.; an area of about 20ft. by 20ft. in the steam engine laboratory; and a long trench through the workshops 110ft. long by 5ft. inside; which all contain tanks, channels, pipes,

and other appliances devoted to the storage, supply or measurement of the water used in the hydraulic laboratory. The arrangement of the whole is shown on Plates II. and III. In the first place, the large tank at the top of the School, a composite structure of steel and iron, 46ft. long by 6ft. 6in. wide and 7ft. 6in. deep, is capable of holding 11,000 gallons of water. It is connected by a 12in. main 338ft. long with the turbines and other appliances in the basement, and by its means a constant head of water up to a maximum of 100ft. can be maintained for the purposes of a test. The design and erection of this tank was not altogether an easy matter. Being situated over the grand staircase, the supports upon which it rests were of necessity 45ft. apart; so that it had to be constructed not merely as a tank but as a girder to support itself. Then again, its great height above the basement and the small door in the tank house through which everything had to be passed necessitated its being made in small pieces; and due credit must be given to Messrs. Glenfield and Kennedy, of Kilmarnock, the contractors, who succeeded in making it staunch and stiff under such difficult conditions. The turbines which this tank supplies are three in number, and each of 20-brake horse power. The general arrangement of the laboratory is shown in Plate IV. and Plate IVa. One is a Girard or impulse turbine with partial admission, radial outward flow and horizontal shaft. The others are reaction turbines of the Thomson or Francis type with horizontal shafts, having radial inward flow and working with draft tubes. On their most economical speed, which is that due to a fall of 50ft., these turbines use about 280 cubic feet or 1,750 gallons of water per minute; but with high heads and slower speeds than the normal, quantities up to 3,000 gallons a minute may be required. At such high rates of consumption of water, the large high-level tank could only keep up the supply for about four minutes; and as the turbines must run for a considerable time in order to get the conditions steady enough for a satisfactory test, means had to be devised for keeping the tank replenished from another source than the Corporation mains; from which it would have cost £3 or £4 per hour to work only one of them. A centrifugal pump was, therefore put in, capable of delivering normally 2,000 gallons per minute against a total head from suction well to tank level of 128ft., see Plate I. To discharge this quantity the pump runs at 950 revs. per minute, and is driven by a continuous rope from a 200 horse power electric motor running at 300 revs. per minute. The pump and motor are, however, capable of being speeded up until the revolutions of the former are 1,200 and then it is capable of delivering 3,000 gallons per minute into the high level tank. This centrifugal pump, constructed by Messrs. J. and H. Gwynne, is of their twin-series type; the discharge of the first pump delivering into the suction of

the second. A similar method of working was invented by Professor Osborne Reynolds; and pumps called Mather-Reynolds pumps have been made on this principle for some time by Messrs. Mather and Platt with three or four, or even more, centrifugal pumps in series, for very high heads. The design of this pump has, I am informed by Mr. Earl, of that firm, recently been very much improved by the collaboration of Messrs. Sulzer, of Winterthur, and very high efficiencies are now attained. The electric motor used for driving not only the Gwynne pumps, but alternatively the two-stage air compressor elsewhere described, was manufactured by the Lancashire Dynamo and Motor Company, of Trafford Park, and designed by Mr. A. P. Wood of that firm. By reason of its special construction with a double armature winding and two commutators, which enable these two windings to be put either in series or in parallel, and by the use of a liquid rheostat in series with these conductors, the widely varying conditions of service to which it is subjected have been successfully met. These conditions include the following :-
Not only must the centrifugal pumps be driven at motor speeds of 300 to 500 and horse powers up to 150; but it must be possible to run the air compressor at any speed from 40 revs. per minute up to 200 or 300, with an approximately constant torque, or in other words, at a horse power varying nearly as the speed. By the use of this electric motor, taking its power from the electricity station in the School, and the centrifugal pumps, a continuous supply of 3,000 gallons of water per minute can be maintained for the purpose of hydraulic experiments; the water after discharge from the turbines, passing over a weir and through measuring tanks to the suction well below the pumps, and from there being returned by them to the high level tank. The cost of the required power amounts to about £1 per hour at the maximum rate of working.

Water Measurement. The turbines discharge either freely or through a draft tube into the flume shown on Plates IV. and IV*a*., and the water is stilled by passing under screens and through perforated plates before reaching the forebay of the sharp-edged rectangular weir, by whose means the quantity flowing is estimated. This forebay is 4ft. in width by 7¼ft. deep and 15ft. in length from screens to weir. The weir itself may be of any width from ½ft. to 4½ft. advancing by ¾ft.; and the head of water over the crest of the weir may reach 2¼ft. The fine hook gauge used for measuring this head was designed and constructed by the Cambridge Scientific Instrument Company. After falling over the weir the water flows through a kind of lock and a sluice valve (on which submerged weir experiments may be made) in to a long trench in the floor of the mechanical workshops, which leads to another forebay opening over the

measuring tanks. These measuring tanks, six in number, each of a capacity of about 600 gallons, are placed in a large excavation in the floor of the steam engine laboratory. As seen in Plate I. they are placed two and two; so that the three square cast iron pipes leading from the forebay just mentioned are able to serve two tanks each. Each tank is supplied and emptied by means of two 15in. diameter lift valves. These valves are operated from an interlocking arrangement of handles by means of high pressure town's water. The handles open and close small slide valves which admit or exhaust the pressure water from the upper or lower sides of small pistons working in cylinders formed in the valve boxes and connected to the valves themselves. It is impossible to admit water from the forebay to any tank so long as the outlet valve on that tank is open.

The water is measured volumetrically by allowing it to fill up to, or rather over, the level of the conical overflow pipe in each tank; when the flow is diverted into the next. The waste from the overflow pipes is caught in a separate tank common to all the six large ones, and so accounted for. In this way it is possible to check the ordinary formula as applied to the weir in the laboratory by actually measuring the water flowing, up to a maximum of about 3,000 gallons per minute.

Vee-Channel. The long trench between the hydraulic and steam engine laboratories was taken advantage of for the installation of a fine and unique vee-channel made of cast iron pieces of rectangular vee-shaped section bolted together to a total length of 110ft. The inside of the channel is carefully planed and the ends of each piece are machined square so as to be accurately in alignment when bolted together. The channel is suspended by screw bolts from channel irons placed across the trench; so that the whole length may be set at any gradient from 1 in 20 to level. For the method here adopted the author is indebted to the ingenuity of Mr. P. W. Robson. By means of the sluice valve in the forebay in the steam engine laboratory it will be possible to work with the lower as well as the upper end of this vee-channel drowned; and it is hoped to make a research on the law of the flow of water in channels under such conditions of accurate alignment, uniform surface friction, and constancy of hydraulic mean depth that further light will be thrown on a very intricate but important problem in hydraulics. Earthenware or other pipes may also be laid at any ordinary gradient in the whole or part of this vee-channel and the laws of flow therein experimentally tested. A special clinometer, the joint design of the author and the Cambridge Scientific Instrument Company, was constructed by the latter, for use with this vee-channel. By its means a uniform gradient of known amount can be attained in every part of the

channel; and injurious springing of the same when raising or lowering by unequal screwing of the suspension bolts avoided.

Turbines. With further reference to the turbines, whose great size, as compared with other such laboratory plants, dictated the scope and nature of the water measuring appliances above described, the Thomson Vortex and the Girard turbines were specially fitted according to the author's specifications with means for the study of the action of the water when passing through them. The turbine wheels may be removed and a dummy or fixed wheel substituted with blades accurately made to the absolute path taken by the water when the turbine is at work, so that an actual measurement of the hydraulic resistances due to surface friction through guide blades and wheel vanes may be made. The head required to cause, say, 280 cubic feet of water per minute to flow through the turbine with the fixed wheel in place will give a close estimate of the above losses; and by moving the fixed wheel into various positions relatively to the guide blades, it is hoped to make some approach to a determination of the loss due to the thickness of the vanes of the moving wheel. It is also proposed to make experiments on the amount of the leakage of water which takes place in the clearance spaces at the sides of the rotating wheel. By placing small vanes at various points in the current of water, the parallelism of the water lines to those of the vanes can be indicated either by external pointers in the guide passages, or by a potentiometer electrical resistance method in the turbine wheel. The horse power developed by these turbines is measured and absorbed by a band friction-brake encircling a pulley with water-cooled rim which can be coupled to either wheel. The net pull of the band is communicated to a floating lever and is partly balanced by a dead weight and partly by a spring, the deflections of which are recorded on a rotating drum driven from the turbine shaft. Thus a record of the variation of the brake horse power during a run can be obtained. For the principle of this method the author is indebted to Mr. A. L. Mellanby. The Thomson and Girard turbines and the friction dynamometer, as also an experimental Pelton wheel of 24in. diameter for heads up to 600ft. were supplied by Messrs. Gilbert Gilkes and Co., of Kendal. This well-known firm entered *con amore* into the question of the special testing appliances projected by the author for these motors, and some of the fittings, such as those for supplying and removing the cooling water for the brake, along the centre of either turbine shaft, are entirely due to the ingenuity of Mr. Gilbert Gilkes of that firm. To him also is due the method of constructing the experimental Pelton wheel 24in. diameter with revolver nozzles and removable buckets. Not only can the best type of bucket be proved by changing them, but by

Crowding them together or setting them further apart around the wheel, the pitch giving best efficiency can be determined. The weir and vee-channel and sluice gates were constructed by Messrs. Heenan and Froude, of Birmingham. The six measuring tanks of composite steel and cast iron (to stand a pressure of 150 lbs. per square inch, when used as compressed air reservoirs) were made by Messrs. George Scott and Sons, of London; and the 15 in. valves, the small hydraulic cylinders, and valve switchboard for these valves were made by Messrs. Isaac Storey and Sons, of Manchester. The second reaction turbine above referred to, and which can be fitted in place of the Thomson Vortex turbine, is by Messrs. Hemmer Bros., of Neidenfels, Germany. It is called by them a "spiral" turbine, and the special interest of it is that it is guaranteed by them to give a specially high efficiency of performance. For hydraulic experiments at pressures up to 600 ft. head Messrs. George Scott and Sons constructed to our designs a special tank of composite steel and cast iron. It is of a form intended to keep the lines of the flowing water as nearly as possible parallel to each other, or in other words to get rid as far as possible of eddying motions. This is absolutely necessary if the phenomena of flow through sharp-edged orifices is to be studied. The 12 in. supply main increases gradually by the interposition of a conical mouthpiece up to the full diameter of 4 ft.; and screens of perforated plates and gauze wire of gradually increasing fineness are placed at intervals across the entire area of the tank. Water can be supplied to this pressure vessel either from the large tank on the roof up to heads of 100 ft.; or, by means of a reciprocating pump (presently to be described) the pressure may be increased up to 300 lb. per square inch, the quantity being then, however, restricted to 300 gallons per minute. By the use of this plant, values of the co-efficients of velocity, of contraction, and of discharge can be determined with sharp-edged orifices up to 3 in. diameter. Measurements of quantity are made by conveying the flow through a switching breeches-piece and the sheet-iron piping to a square basin. This basin, having been carefully calibrated by filling it with weighed quantities of water, and taking the corresponding heights with the hook gauge, becomes a measuring tank, having a capacity of about 800 gallons per foot, or 5,760 gallons in all. With the high-pressure tank it is intended also to make experiments on the flow of water through cocks and valves of various types; and through sudden enlargements and contractions, as well as elbows and bends in pipes. For low heads there is fitted in connection with this jet-tank a large vertical stand-pipe with internal overflow, constructed telescopically so as to allow of the upper edge being set to discharge at any required height within the limits of the apparatus. Thus if the loss of head due to

the flow through an elbow or bend fitted on the front of the jet-tank is required, the overflow in the stand-pipe is set to a head corresponding to the velocity required to be maintained through the bend, and a little more water supplied from the high tank than is flowing through the bend, so that a fairly constant small overflow takes place in the stand-pipe accompanied by only infinitesimal changes in the head of water. Constant pressure in the jet-tank under high pressure is maintained by the uniformity of speed of the pump supplying the water, together with an adjustable spring relief valve discharging from the upper part of the jet-tank, where the latter is kept filled with compressed air from a reservoir supplied by one of the air compressors.

The Experimental Pump. The exhibits at the Paris and Glasgow Exhibitions of high-speed reciprocating pumps coupled directly, *i.e.*, without intermediate gearing, to electric motors, will be in the memory of members. Professor Riedler, who, along with Professor Stumpf, of Berlin, designed some of these pumps, has long been an advocate of high-speed pumps and air compressors with controlled valves. As there seemed to be a general indisposition on the part of English pump makers to adopt the high-speed principle for pumps, the author obtained the sanction of the Committee to the installation in the hydraulic laboratory of a direct connected "express" pump on the lines of those above mentioned, for the purpose of enabling experiments upon their behaviour to be made in Manchester. The pump is normally a differential plunger pump with 7in. and 5in. diameter plungers, having 12in. stroke. But it is so arranged that it may be worked with either plunger single-acting, and that the stroke may be varied from o to 12in. It is direct connected, through a flexible coupling, to a 120 H.P. 4-pole direct current motor; of which, by means of a large air-cooled rheostat, the speed may be varied between 50 and 300 revolutions per minute; the brake horse power varying simultaneously from 20 to 120. It may be remarked that the rheostat cost nearly as much as the motor; but that it has almost justified its purchase already in connection with another series of experiments for which the motor has been used. Four different types of valves were projected for experimental use in this pump; and great credit is due to Messrs. Frank Pearn, the makers of the pump, for the way in which they carried out the ideas shown in the preliminary design which was carefully thought out for the author by Mr. A. L. Mellanby. It will be seen that the mass of the valves of all the types can be changed by affixing to them lead weights, and that the amount of lift can be varied from without the valve chambers. The motion of any of the valves can be communicated by arms, whose ends move with them, to a rocking-shaft fitted across the valve-box, and passing through a stuffing-box in its sides.

In this way the actual movements of the valves throughout the stroke of the plunger can be observed outside the pump, and recorded by a pencil on an indicator barrel, if so desired; so that the action of the various types as affected by variation of loading and speed can be studied. It may be that in the next fifty years the reciprocating type of pump will become quite obsolete, and will be found only in museums, having been superseded by the compound centrifugal pump of the type invented by Professor Osborne Reynolds. Yet close attention to the details of design of reciprocating pumps, with consequent improvement of their working, and an increased speed of running accompanied by diminution of size and first cost, may help to retard the date of their extinction. In the same way the advent of the electric light, instead of, as was thought at first, leading to the entire disappearance of gas as an illuminant, has greatly stimulated its improvement, and the competition between the two is to-day probably keener than ever before. Higher speeds and better volumetric and mechanical efficiencies must then be aimed at for reciprocating pumps; and it may fall to the lot of the experimental pump in this School to help in their improvement in these respects. In seeking to improve a mechanism the first desideratum is a knowledge of the laws of its action; and for the improvement of the design of pump valves, the laws which govern the frictional losses through them, the correct timing of their opening and closure, and the effect of size and shape upon their silent working at high speeds must be investigated. A beginning has been made by several experimenters on the Continent, notably by Professors Bach, Riedler and Stumpf; but until quite recently the researches were restricted to single small valves, not more than two inches in diameter. In order to extend this work and apply it to large single valves and to groups of small ones, the following arrangements were projected in connection with this pump. The stand-pipe for low heads already referred to can be connected to the pump suction, and the water allowed to flow through either the suction or delivery valves or both consecutively at the same speed as it will have when the pump is working. After leaving the delivery valve box the water rises in a conical overflow vessel, and the difference between the levels of the water in this and in the stand-pipe gives the head lost by surface friction and bends in the pipes, valve and pump chambers, and by valve resistance. If now the same experiment be carried out with all valves removed, and the water still flowing through at the same speed, the difference of the heads in the two cases will be that lost by hydraulic resistance of the valve alone. Gear is also provided on the pump on a plan suggested by Messrs. Pearn for closing the valves mechanically. This consists of screw gearing driving a lay shaft on which adjustable cams

are formed. Motion is communicated by the levers, springs, and push rods to the valves, which are thus closed at the proper time. Opening of the valves, however, takes place automatically. When running at the slower speeds the pump draws its water from the square basin (above mentioned), to which it returns after passing through the jet-tank, having previously been discharged under the desired constant head through an appropriate sharp-edged orifice. At high speeds the suction valves of these pumps work under a small head, and it is therefore arranged that in that case the pump shall draw from the 12in. main connecting to the high-level tank; a large overflow regulating valve keeping the pressure constant.

3.—MACHINE TESTING LABORATORY

A floor space of 40½ft. × 25½ft., or 990 sq. ft., is devoted to machine testing, in the same room as that in which the hydraulic apparatus is installed. The testing of the kinematical and dynamical properties of the machinery of transmission, such as belt, rope, and chain drives; spur, bevel, worm and screw gearing; and the efficiency of machine tools are the objects to which this laboratory is devoted.

The machines and pieces of apparatus in this laboratory on which tests may be carried on comprise : Friction testing machine, for the determination of the co-efficient of dry friction of different metals at various speeds, and under various pressures up to that of seizing. Apparatus for the study of the action of a Porter pendulum governor by means of a Horn tachograph and an electric motor; the governor-sleeve itself operating the rheostat handle. Drilling machine, adapted for testing the relative hardness of cast iron and steel, fitted with autographic recorder. Apparatus for testing the frictional resistance to slipping of a belt upon various pulley surfaces. Means for the calibration of a 10 H.P. electric motor, for use as a transmission dynamometer; and apparatus for testing the accuracy of alignment of a lathe.

4.—THE GAS AND OIL ENGINE LABORATORY.

Two gas engines and two oil engines each of 20 B.H.P. are installed in this laboratory, which is a fine room 29ft. by 53ft. in the basement. The general arrangement of the plant in this laboratory is shown in Plates V. and VI.

Gas and Oil Engines. One of the gas engines, by Messrs. Crossley Bros., has an air compressor for low pressures driven from its crank pin, the capacity being such that air enough for the supply of any of the other three engines may be obtained from it. This air, being delivered into an air holder of 170 cubic feet capacity, from which the engines draw their supply, is measurable by counting the number of strokes of the compressor made during the engine trial and by

knowing the volumetric efficiency of the compressor. In short the air compressor becomes an air meter. Back explosions, which constitute the danger of the method of measurement with an air holder, are provided for by a tallow blow-off valve as used by Professor Burstall, of Birmingham, in his work for the Research Committee of the Mechanical Engineers. An alternative method of air measurement is provided by three large reservoirs each of about 100 cubic feet capacity, which can be filled with air at high pressure
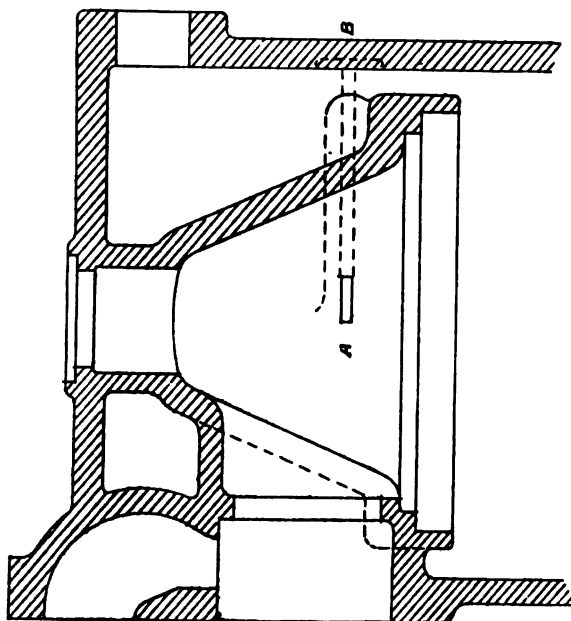
Fig. 5.

Fielden and Platt Oil Engine (Thermometer Pocket).

(from the large two-stage air compressor in the steam engine laboratory); and after settling down to a known temperature and pressure in any one of them, can be allowed to flow out as required into the air holder from which the gas and oil engines draw. It can easily be shown that for a given accuracy of the temperature and pressure measuring instruments, the quantity of air used can be more exactly determined when passed through a reservoir at a high than at a low pressure. The other gas engine is by the National Gas Engine Co., of Ashton-under-Lyne, and is specially fitted with thermometer holes in the walls of the cylinder and clearance space

for the purpose of their temperature determination under the different conditions of running. It is the mean temperature across the thickness of the walls in different parts of the cylinder which will be thus determined; not that of the inside surface, which probably varies very considerably above and below this mean during the course of a revolution or cycle. The latter temperature can only be determined by somewhat delicate electrical measurements in connection with thermo-electric junctions placed in small holes drilled nearly through the walls from the outside; as was done by Professor Callendar and the author with a 50 H.P. steam engine some years ago in Montreal. If curves of surface temperature throughout a cycle could be plotted for the principal portions of the
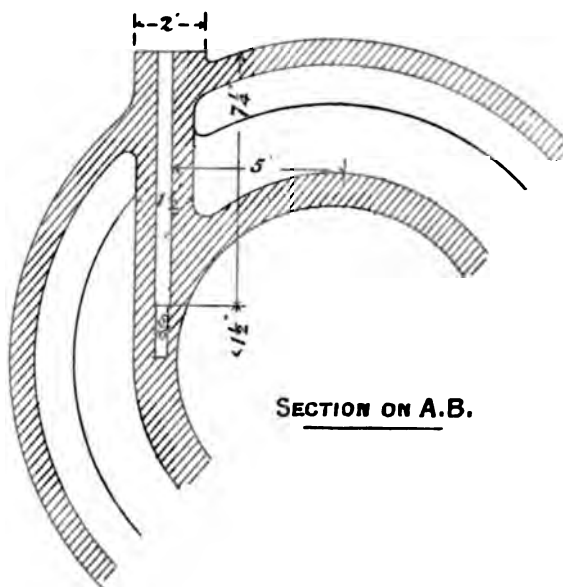
Fig. 6.

Fielding and Platt Oil Engine (Thermometer Pocket).

cylinder wall of an internal combustion engine, the quantity of heat given up to them by the working substance not only during the whole cycle but during the various phases of the cycle could be determined; and great light would be thrown upon such important questions as the variation of the specific heat of the mixture with temperature, the rate of flame propagation, and the laws of heat conduction to a metal surface as depending on temperature and density; and the existence and amount of dissociation during com-

bustion. The two oil engines in the laboratory are similarly fitted; that by Messrs. Richard Hornsby and Sons, Grantham, with specially designed gun-metal thermo-junction protectors, and with an alternative pair of heavier fly wheels for speed fluctuation study.

The engine by Messrs. Fielding and Platt, of Gloucester, has their very latest type of vaporiser fitted, and has thermometer protectors in the walls as shown in the Figs. 5 and 6. A 20 B.H.P. dynamo by Messrs. Crompton and Co. can be attached by a Raffard flexible coupling to any one of these four engines for braking purposes; and as the current so obtained is delivered to a liquid rheostat, a perfectly steady load can be maintained for any desired length of trial. Alternatively, if it is desired to study the interaction of governor and fly-wheel and the fluctuations of speed due to varying loads, whether suddenly or gradually applied, this can be very conveniently effected by the use of the rheostat. Two of Dr. Horn's well-known tacho-graphs are available for such work; one shows variations of speed so small as one-fifth, the other as one-half of one per cent. The temperature of the walls, of the exhaust gases, or of the jacket-water can be automatically recorded by the use of platinum thermometers connected to Callendar recorders; and it is hoped also to record the varying temperature of the working substance during the cycle, by the use of a cycle contact maker, and a thick and thin wire ther-mometer on the plan suggested by Professor Callendar himself.

A fine wet-meter by Messrs. Sawers and Purves, and a standardising holder by J. and J. Braddock, are provided for the accurate measurement of quantities of air or gas. It may safely be said that there is no more complete laboratory outfit in existence for the experimental study of the gas and oil engine than the one just described; this state of things being due to the judicious liberality with which the Technical Instruction Committee sanctioned the author's proposals.

Ammonia Refrigerating Plant. In the same room are located two refrigerating plants, each of a capacity sufficient to manufacture one ton of ice per day of 24 hours. One of these was supplied by Messrs. The Linde British Refrigerating Co., Ltd., and is on the ammonia system. It consists of an ammonia compressor of the horizontal double-acting type, belt-driven from the line shafting in the laboratory. Three special pistons are supplied for varying the clearance volumes from the normal to ⅛in. or ¼in. at each end; and the barrel and covers of the compressor have fittings and openings in the walls for inserting thermometers. The valves are fitted with special indicating gear for studying their action. The piston rod is bored down the centre to permit of the insertion of a Callendar thin wire thermometer for measuring the temperature of the

ammonia during compression and evaporation. Thermometer fittings are also arranged for on the inlet and outlet pipes to the compressor for taking the temperature of the ammonia before and after compression. The ammonia condenser is of the submerged type and consists of three different coils of lap-welded wrought iron tube wound each in one length so as to avoid inaccessible joints. These coils, each of $1\frac{3}{16}$in. bore, are of 200ft., 150ft. and 100ft. total running length; the first named of 78·6 square feet area being the normal coil for this size of compressor. Instead of the condensing water being allowed to flow vertically past the coils, it is arranged, by having sets of half diaphragm plates of galvanised sheet iron for each coil, which are inserted between each thread, that it shall circulate spirally with or against the coil in one continuous passage from bottom to top. The object of this arrangement is to secure a definitely directed circulation of the cooling water at a known speed outside the ammonia coil; so that the effect on the rate of heat transmission across it of different speeds of circulation may be observed and recorded. Thus it may be found that an abnormally small coil with a high rate of water circulation is just as efficient for cooling purposes as the larger coil with the slower speed. The evaporator is of quite similar design so far as the coils and diaphragm plates are concerned; but has in addition a special watertight jacket space $\frac{1}{4}$in. wide around the sides, and a space at the bottom fitted with slag-wool. The jacket-space is to be kept at a constant temperature by a continuous supply of water, so that by measuring the quantity supplied and its fall of temperature during passage through the jacket, the loss of refrigerating effect due to radiation from the surroundings may be closely allowed for. The special brine pump is of great size, being capable of delivering as a maximum 1,200 gallons of brine per hour. This pump has an adjustable length of stroke and three speed cones, so that any rate of circulation of brine within the above limit can be obtained. It is driven by belt from the laboratory shafting. An ice tank to hold 20 terned steel moulds for blocks of ice, each weighing about 56 lbs., is part of the installation. This tank is fitted with a propeller for circulating the brine amongst the ice moulds, the propeller being driven by belting from the line shafting. Mr. T. B. Lightfoot, of the London Linde Company, took the greatest interest in the designs and execution of this plant. The author takes leave here to express his thanks to him and the other members of his staff for the trouble they took in carrying out and improving upon his suggestions.

Carbonic Acid Refrigerating Plant. The second plant is one in which carbonic anhydride is used as the working fluid on the system of Messrs. J. and C. Hall, of Dartford. In the standard type of this

machine the evaporator (or refrigerator) occupies a central portion of the base of the machine, and is inside the condenser. It is insulated from the latter by means of double walls filled in between with hair felt. In the experimental plant the evaporator is a quite separate vessel from the condenser; and both are fitted so that three separate lengths of coil may be used. The way in which this is effected is shown in Fig. 7, from which it is seen that the carbonic acid coils, three in number, are formed to the same helical pitch and diameter as the brine or water circulating coils, and threaded within them. This method is the invention of the late Mr. Alexander Marcet, of the Dartford firm. In this way it is possible : (1) Keeping the brine circulating at an invariable speed, to study the effect of different areas of coils upon the rate of evaporation or condensation of the CO_2. The carbonic acid may be forced through the spiral coils, one, two, or three abreast; the speed of circulation and the area of pipe per pound of working fluid being thus varied at pleasure. (2) Keeping the speed of the carbonic acid and its coil area both constant, the effect on the rate of transmission of heat through the coil may be studied as affected by different speeds of brine circulation. The large brine pump of the Linde plant can therefore be diverted for use with the Hall refrigerator so that speeds of the brine up to four or five times the normal may be attained. The cooling effect of the brine circulated (normally to a cooling chamber or to an ice-making tank) is to be measured by the heat it takes up from a coil of wire heated by an electric current, on the plan used by Professor Ewing, at the Engineering Laboratory, Cambridge. Thermometers can be inserted at various points in the circuit, as also in the compressor cylinder walls; provision for this having been made in the supply by Messrs. Hall of a special compressor casting with pockets in three places in the ends and side of the cylinder. This compressor is driven by belting from the line shafting of the gas and oil laboratory, and can therefore be operated by any one of the engines. It can also be driven by the Crompton dynamo working as a motor from the electric mains of the building lighting and power circuit.

5.—MATERIALS TESTING LABORATORY.

This laboratory has a floor area of 1810 square feet (74 × 24), and is devoted to the testing of the materials of construction, such as iron, steel, copper, the alloys, stones and masonry, bricks and brickwork piers, timber, and the parts of machines and structures. The general arrangement of the laboratory is shown on Plate VII. The Board of Trade does not accept, as sufficiently accurate, tests made in tension or compression with an ordinary hydraulic press. For rough tests it is sufficient to find the load on the test piece by simply multiplying the ram area by the gauge pressure,

but a considerable uncertainty is introduced in that case, especially at light loads, by the cup-leather or gland-packing friction. Testing machines for accurate work have therefore invariably a means for actually weighing the load on the piece which is being tested. A hydraulic ram usually exerts the pull or thrust on one end of the specimen, whilst the other end is connected by links to a lever (or system of levers), upon which a rolling weight of known amount is adjusted to exactly balance the force which the test piece is sustaining. Thus the net pull is known, and the unknown frictional force eliminated.
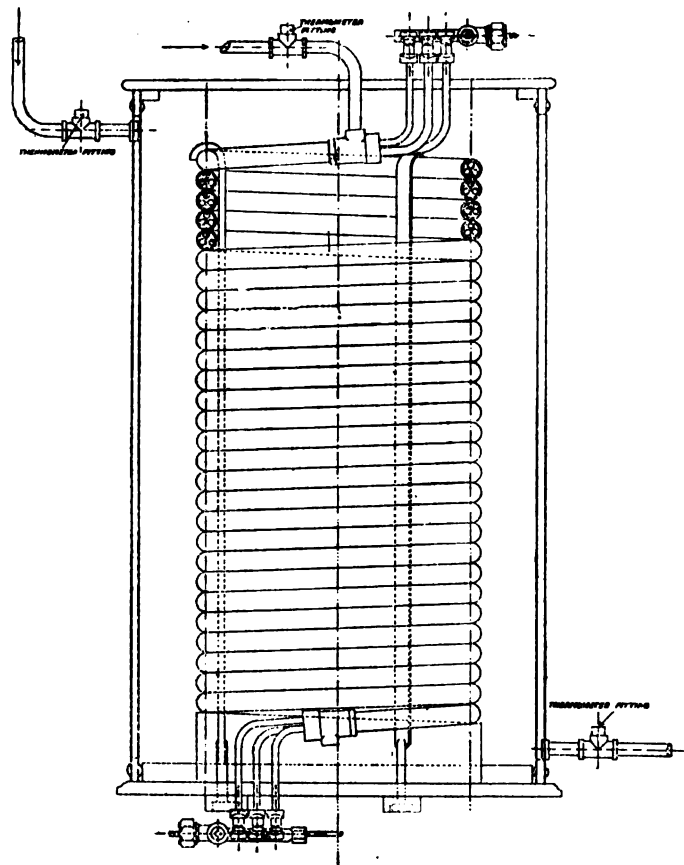
Fig. 7.

Horizontal Wicksteed Testing Machine. A very usual type of testing machine in this country is that designed by Mr. J. H. Wicksteed, and manufactured by Messrs. Joshua Buckton and Co. The machines of this firm, with a single lever, are made up to 100 tons capacity, the specimen being vertically disposed with the pulling cylinder below and the lever above. Horizontal machines in which the specimen and lever are both horizontal usually have a bell-crank lever interposed between specimen and main weighing beam. An example of this type of machine of 50 tons capacity is installed in this laboratory. This type of machine is well known and need not be described in particular. An attachment was, however, designed and fitted by Mr. Wicksteed, at the request of the author, for calibrating the machine at any time during its period of service by applying dead weights of known amount. This consists of a right-angle lever and a cross beam, from which two tension rods depend into trenches in the floor of the laboratory. In each trench is placed a bogie, running on rails, loaded with ten 1-ton weights. The weights are applied two tons at a time by being suspended from each end of the cross beam in succession, as their supports are screwed down out of the way by handwheels on the bogies. The vertical pull of the dead-weight is converted into a horizontal thrust against the knife edge crosshead of the machine by means of the knee lever; a piece of hard steel being interposed resting on two rollers. By these means a load of ten tons can be actually imposed on the lever system at any time, and the reading of the jockey weight on its steelyard verified. The levers are free to swing all the time, and the sensitiveness may also be tested by this method.

Amsler-Laffon Testing Machines. Another type of machine exemplified in the laboratory is that elaborated by Professor Tetmayer, now of Vienna (formerly of Zürich) in conjunction with the firm of J. Amsler-Laffon and Son, of Schaffhausen, Switzerland (Fig. 8). In these machines the load on the specimen is determined by multiplying the area of the hydraulic plunger by the pressure acting upon it. No error due to cup-leather friction is introduced, however, as the plungers are not packed, but simply float in thick oil, such as castor oil, which prevents metallic contact between ram and cylinder, and is allowed to leak slowly past the former. Great care is taken in boring the cylinder and machining the ram to get a fine fit; and, when considered necessary, the ram may also be rotated to and fro in the cylinder during the test so as still further to eliminate any small friction there may be in the axial direction. The principle underlying this method of working is due to Amagat; and is very commonly employed for gauge and indicator-spring testing machines. It is well known to engineers that a shaft rotating in horizontal lubricated bearings will very readily move endwise. The
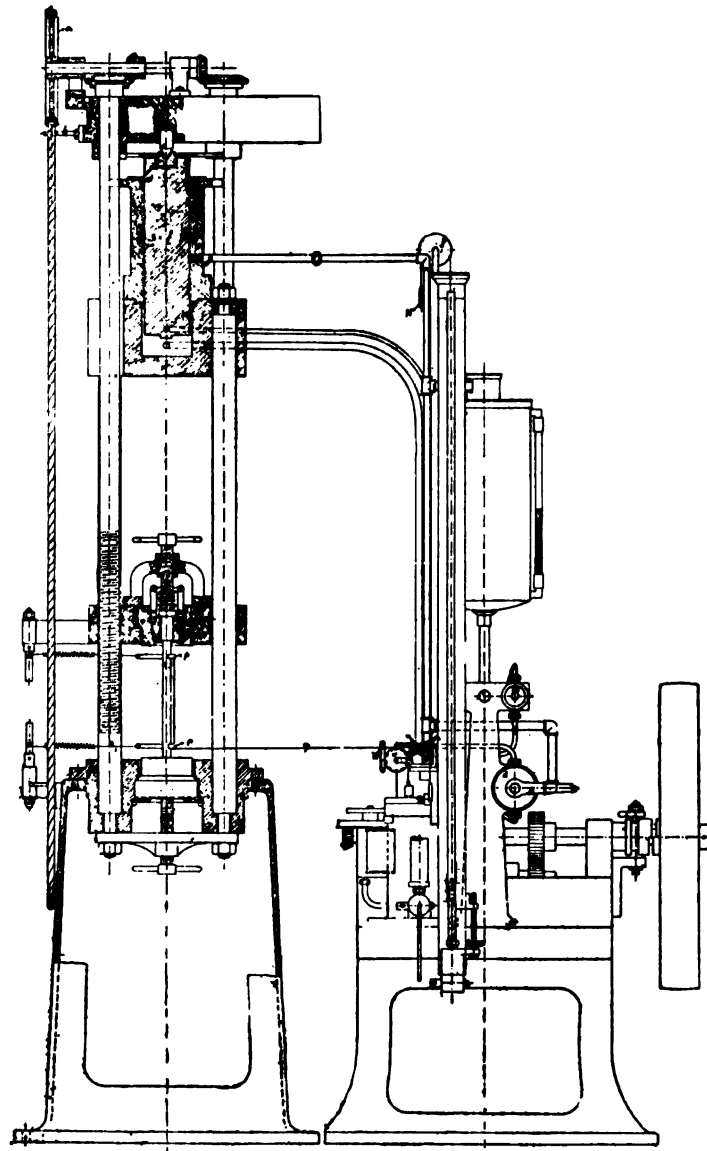
Fig. 8.

25-ton Tension Testing Machine, by Amsler-Laffon.

smallest force is sufficient to induce a slow axial motion in such a rotating piece. The reason for this is obvious if we remember that the direction of the force of frictional resistance which a body opposes to motion is exactly in the opposite direction to that motion, so that the force required to produce axial motion bears the same proportion to the force producing circumferential motion as the axial speed bears to the speed of turning of the surface of the piece.

In the Amsler-Laffon testing machine this principle is applied not only in the main pulling cylinder, where the ram can be rocked to and fro while under pressure, so as to eliminate axially directed friction, but also in the pressure reducing apparatus for enabling the high pressure in the pulling cylinder to be read off as that due to a column of mercury in an open tube about six feet long. As shown in Fig. 9, the pressure reducer, a pipe leading from the pressure cylinder connects to the flange A and produces the same pressure in the space B as in that cylinder. During working, valve W is closed; it serves for unloading the specimen, and emptying the pulling cylinder of oil, viâ the pipe X to the oil reservoir. The pressure in B tends to press pistons C and D down. The sleeve D can be placed in one or other of two positions. If its collared end rests on the bottom of B, the ratio of areas is that of the inner piston C to the ram E; if on the other hand, piston E is raised so that the bottom end of D rests upon it and is clear of the bottom of B, the ratio of areas is obviously that of piston D to ram E. Ram E floats upon a thickness of oil which rests upon quicksilver, connected by pipe H and cock Q to the mercury column I. For small specimens, the pistons C and D press together against E; for large specimens, ram E is lowered by withdrawing oil from cylinder G by means of cock L, and hand-pump K, until D's collar rests on the bottom of B. The position of E, and the reducing ratio are indicated by the little rod S. Two scales, one on each side of the celluloid mercury holder or pipe I, are provided for the two cases. The float M shows the maximum reading attained during a test. Pressure is applied by a rotary hand-pump, so that each machine is quite self-contained.

The 25-ton tension, and the 30-ton beam-bending machines in the laboratory are operated by a rotary pump; whilst the 30-ton compression machine is put in operation by a small ram, worked by a handle and screw. It also has its own pressure reducer and mercury column. These machines have proved themselves handy and accurate; although the pump connections seem unnecessarily complex.

Compression Machine. The third method of eliminating cup leather friction in the measurement of the load on a test piece, which is exemplified in this laboratory is that in which a diaphragm is used

in conjunction with a mercury column. This method, which has been strongly advocated by Professor A. Martens, of the Prussian Government Testing Establishment at Berlin, has been here applied to a compressive machine for loads up to 750 tons. The machine itself consists of an ordinary cotton press as used in this district modified to admit a diaphragm. A strong circular casting is placed upon the straining beam between the pillars at the lower end of the
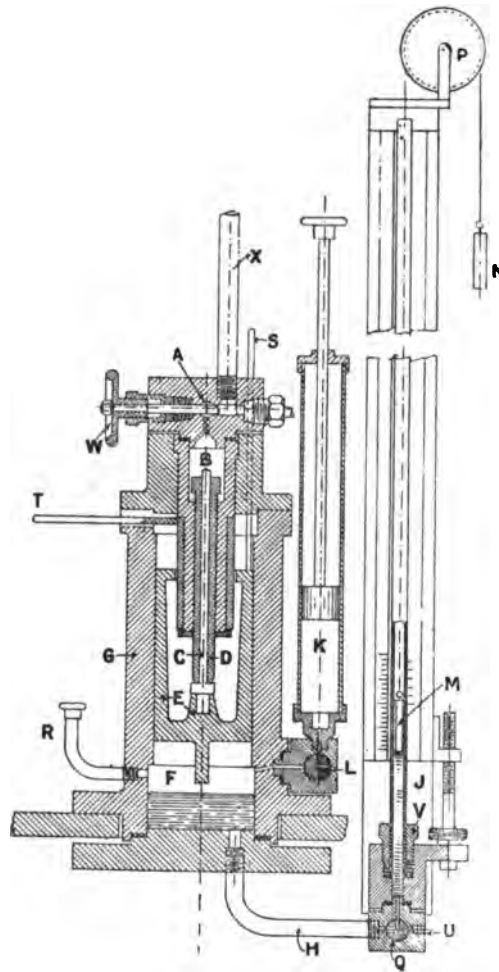
Fig. 9.

machine. The platen carrying the specimen to be tested rests upon a ram fitting the bored interior of this circular casting accurately.

A sheet copper diaphragm connects the ram to the casting and confines a small quantity of rather viscous fluid below it. This fluid gives to the top of a glass gauge fitting which it half fills; the lower half being occupied by mercury. This mercury is supplied from a large strong vessel below and has a connection to a mercury column 180ft. long placed in the elevator well of the building. The pressure below the diaphragm is thus indicated by the height of the column of mercury in the tube, and as this pressure may reach 600lbs. per square inch, and the diaphragm is 3ft. in diameter, a very consider-able load may be sustained and measured within the range of the mercury manometer. Special apparatus, the joint design of Professor H. L. Callendar, F.R.S., and the author, have been provided on the machine, enabling the diaphragm by its small rise and fall, not only to automatically adjust the height of the mercury in the column to the pressure at every moment exerted by the specimen, but also to record this pressure upon a rotating drum by the use of a Callendar recorder, as made for platinum thermometers.

In this way the only duties of the operator are to apply the load at the desired rate by admitting pressure water above the ram, and to take observations of the compression suffered by the specimen as the test goes on. The celebrated Emery testing machine was constructed, as is well known, on the diaphragm principle; but in the experience of the author the sensitiveness of the weighing apparatus was carried to such a degree that one operator was constantly employed in attending to that part of the test alone, and another had to be in attendance upon the pulling cylinder and the extensometer. Water at pressures up to one ton per square inch is provided for this and the 50-tons Wicksteed machine by an accumu-lator and intensifying pump, which works automatically, from the 1,100 pounds City hydraulic mains. In connection with the design of the various plants for this new School the author desires to acknowledge his indebtedness to the ability and untiring energy of Mr. P. W. Robson, who acted as his chief assistant throughout. His sound practical views and skill as a designer were of the greatest benefit during the course of the work.

In concluding this necessarily somewhat curtailed description of so extensive a laboratory equipment, one question of a practical character naturally arises in the mind :—*By whom is the extended programme of experimental work indicated by such an equipment likely to be carried out?* Physical limits are set to the powers of even the most liberally endowed staff, and the possibilities for carrying out useful research work with such students as now usually

attend our Technical Schools—consisting, as they do for the most part, of mere schoolboys and raw, untrained youths—are very restricted. Help must be looked for from those who will most directly benefit from the results to be obtained—the engineering employers.

It is earnestly to be hoped that, conjointly with the unification of educational authorities at present taking place, the leaders of industry will make their voices heard and their influence felt in arranging for some more rational system of engineering education than what has hitherto been possible. The plan which the author believes, from his experience in the workshop and in the college, to be the best, is that in which a term of workshop practice, accompanied by private or other study of elementary mathematics and science, precedes entry upon the college course. A youth can very well learn to chip, file and turn, to make patterns and castings, and to fit and erect a machine or engine without any knowledge of the theoretical principles of engineering; but it is a hopeless task, on the other hand, to try to teach engineering theory, or to attempt experimental work of any but the most elementary character with boys fresh from school, who do not know the names or the functions of even the most elementary parts of machines. The method now almost universal of accepting such youths in Technical Schools is largely a policy of expediency; and has resulted from the conditions prevailing in industrial life, whereby the older the boy is the greater is his market value. All that it has hitherto been possible to do with such a student is to teach him science and drawing, and to explain to him what the commoner machines are for, how they work and what are the names of their various parts. If engineering employers consider this a desirable consummation to be aimed at, then so-called Technical Schools will no doubt be continued and maintained to carry on this drudgery; they ought, however, to be called trade schools, as more truly indicating their real character. The author is bound to confess that he is unable to see any advantages, at all events to the nation at large, accruing from this system. No doubt it is better for the employers that the process of sieving out useless material should be done in Technical Schools at the public cost rather than in the workshops at their expense. This form of argument must also receive due consideration, for the object of a workshop is to make a profit on the capital invested in it. The author therefore wishes to put the matter on tnis very ground of practical profit and loss; and to assert that it will be found to be a remunerative investment to an employer if he will choose one or two of his senior apprentices who show aptitude both in the workshops and at their evening studies; and by enabling them to attend a Technical High School, such as the City of Manchester now possesses, for two or three sessions, he will endeavour to secure a man not only highly trained in

engineering theory; but specially skilled in the carrying out of experimental research work directly connected with industrial processes.

PLATE A

STORES

GAS & OIL ENGINES

SMITHY

FUEL

FOUNDRY

BOILER HOUSE

LUBRICATION TESTING

ENGINEERING WORKSHOP

HYDRAULIC & POWER TRANSMISSION LABORATORY

GENERATING STATION

STEAM ENGINE LABORATORY

TOOL ROOM

BENCHWORK

BICYCLE ROOM

SPINNING ROOM

LAVATORIES

MATERIALS TESTING LABORATORY

WEAVING & OTHER POWER LOOMS

WEAVING PREPARATION ROOM

ELECTRICAL LABORATORIES

ELECTRO-CHEMICAL ENGINEERING
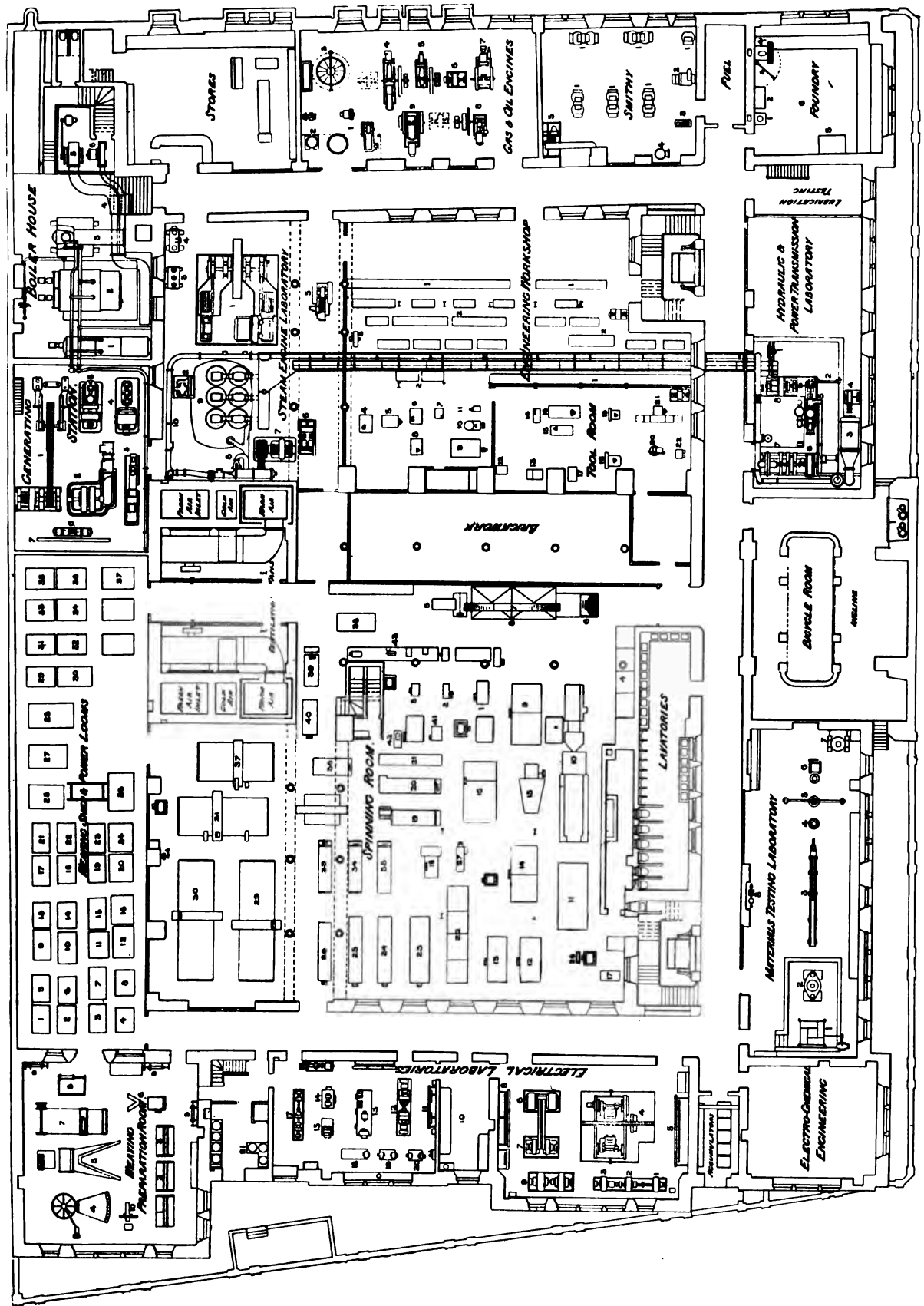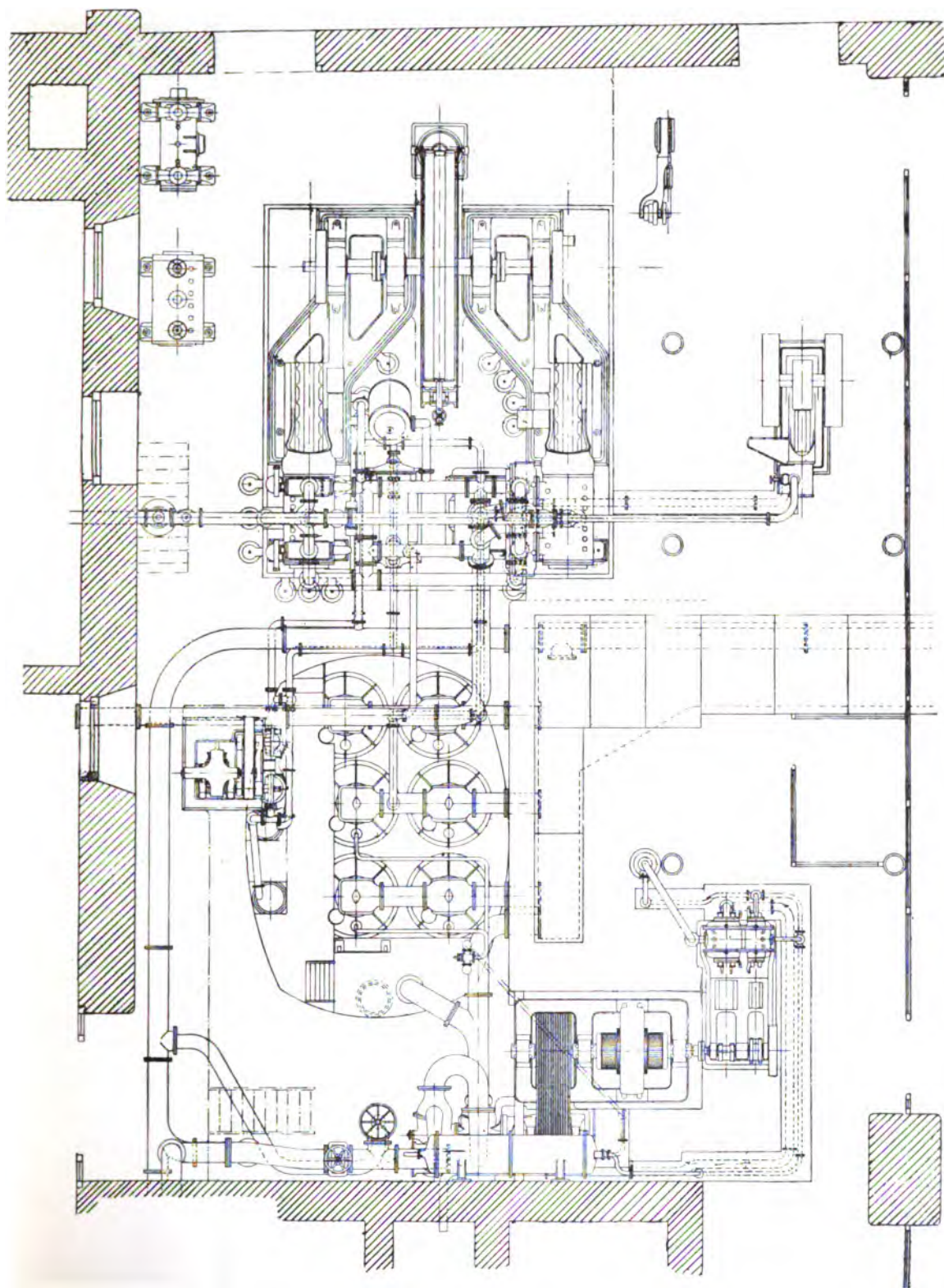
Plate I.

PLAN OF STEAM ENGINE LABORATORY.
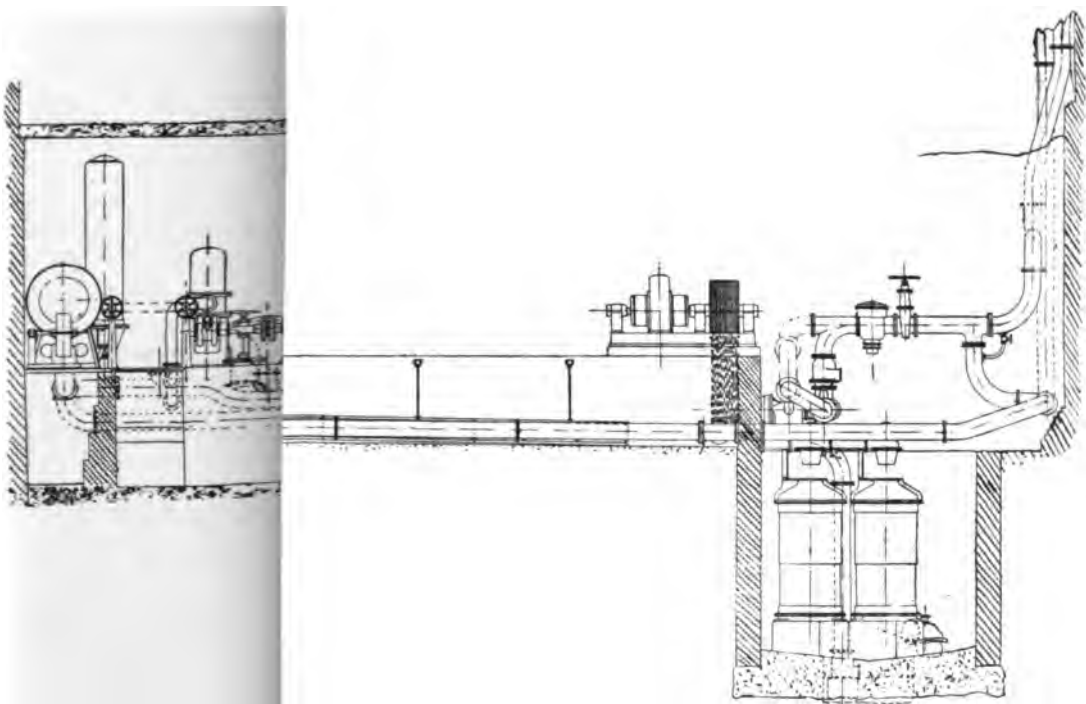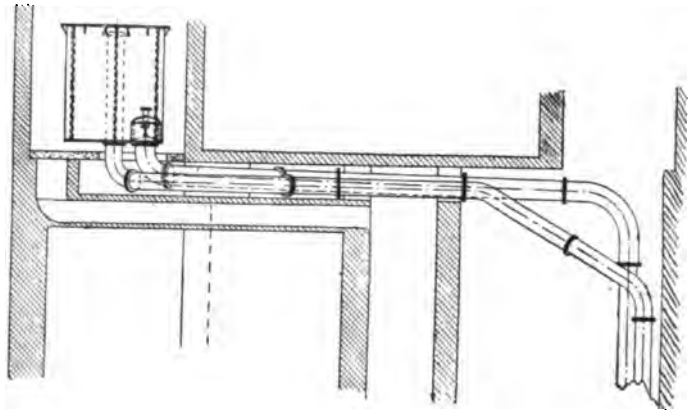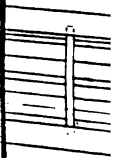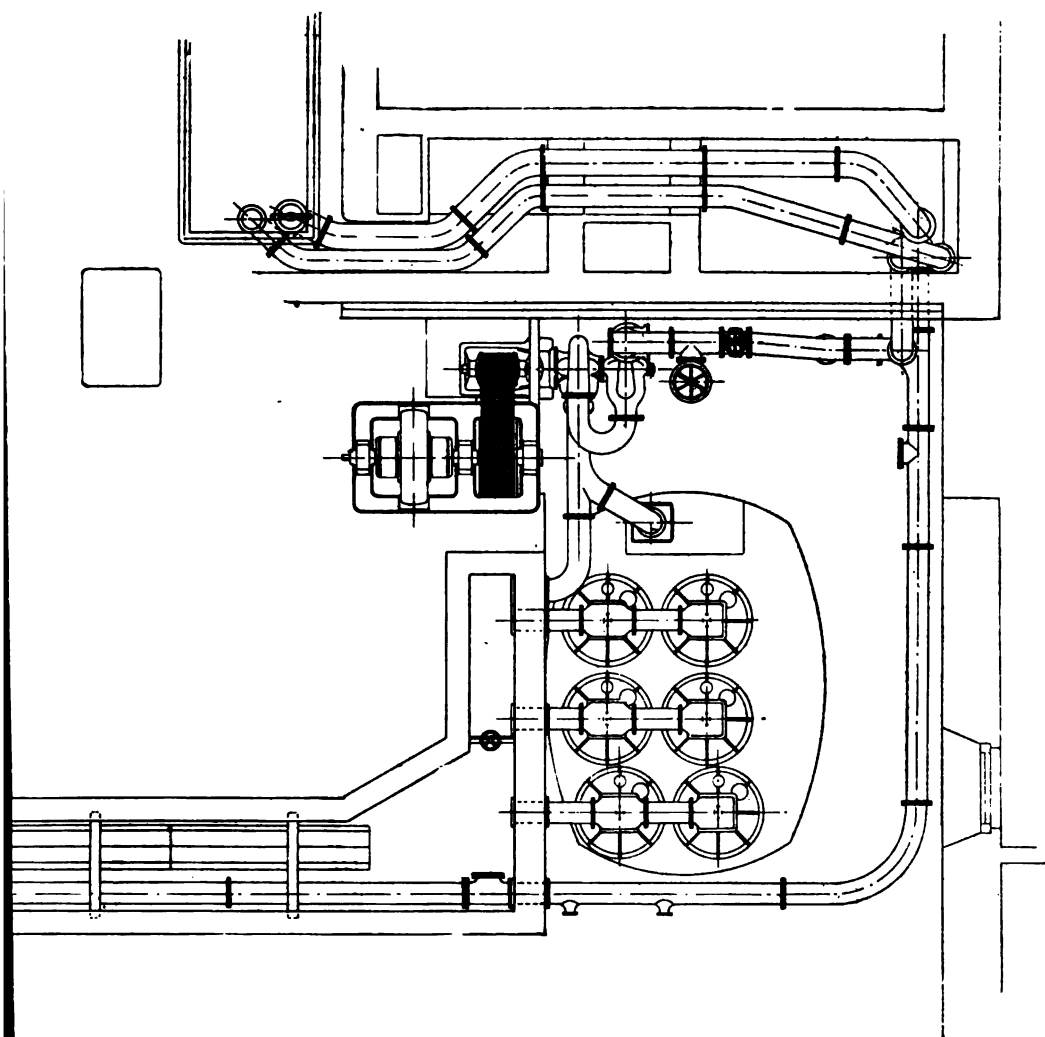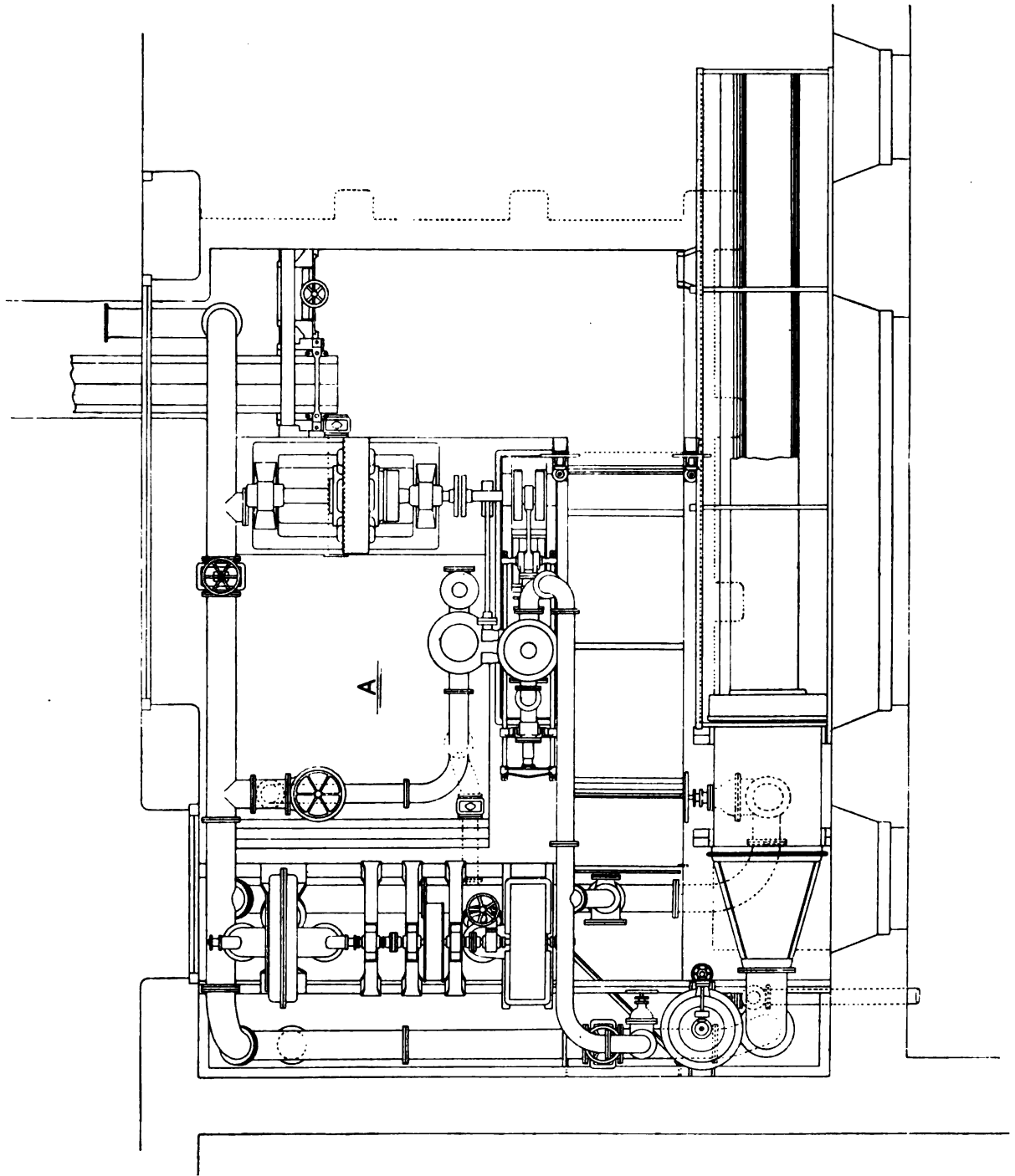
PLATE IV.

A
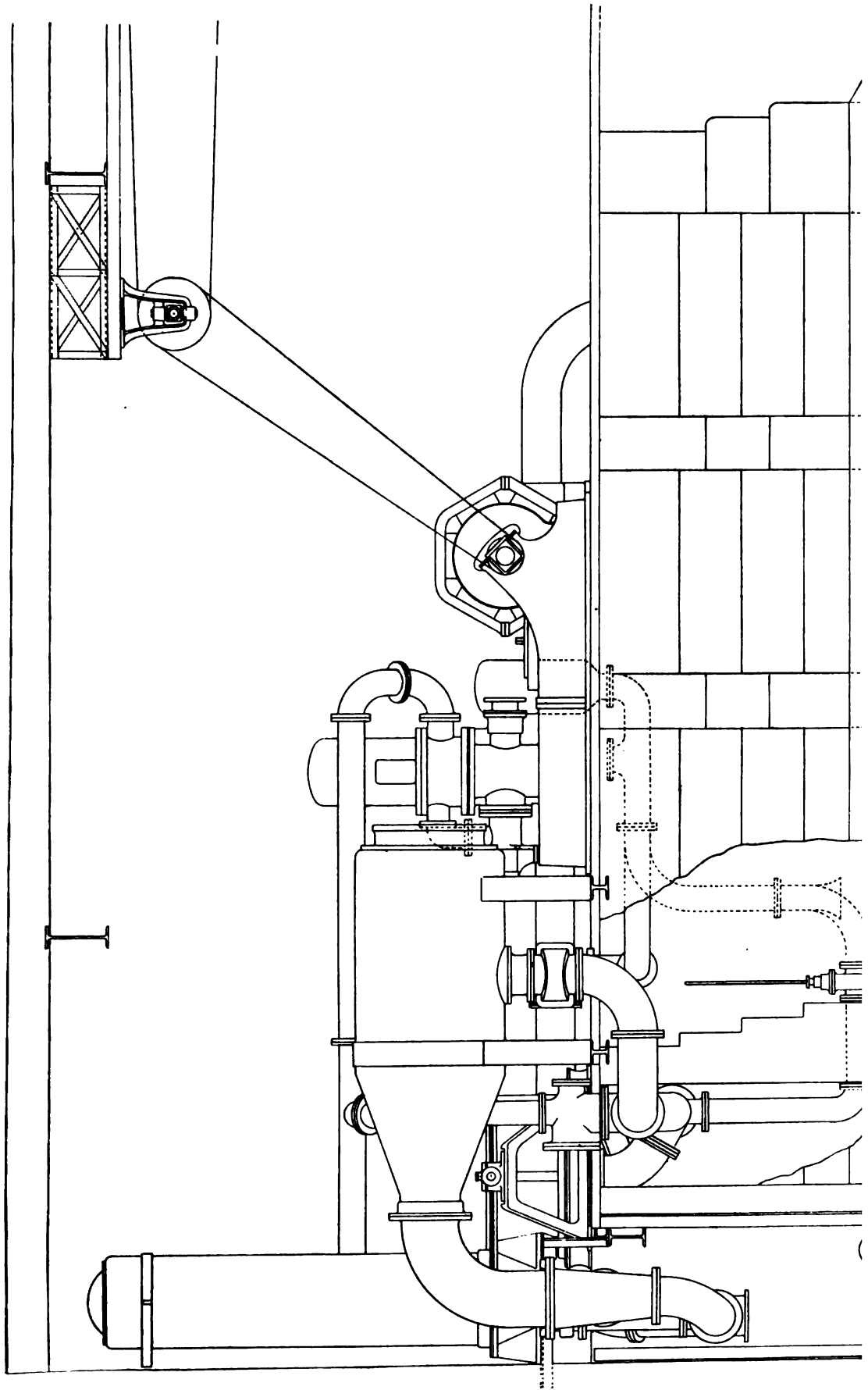
PLATE V.
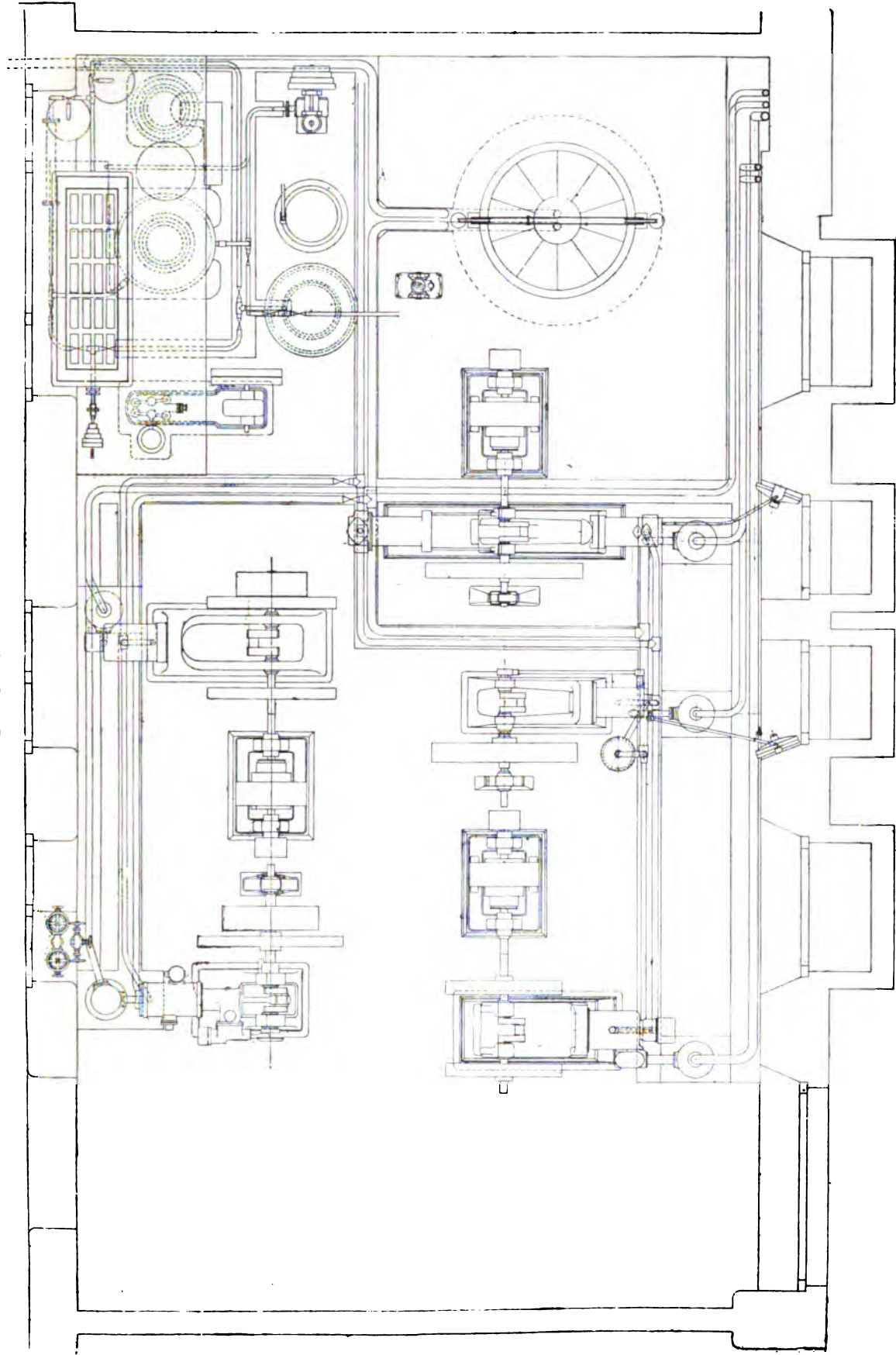
GAS ENGINE LABORATORY (PLAN).
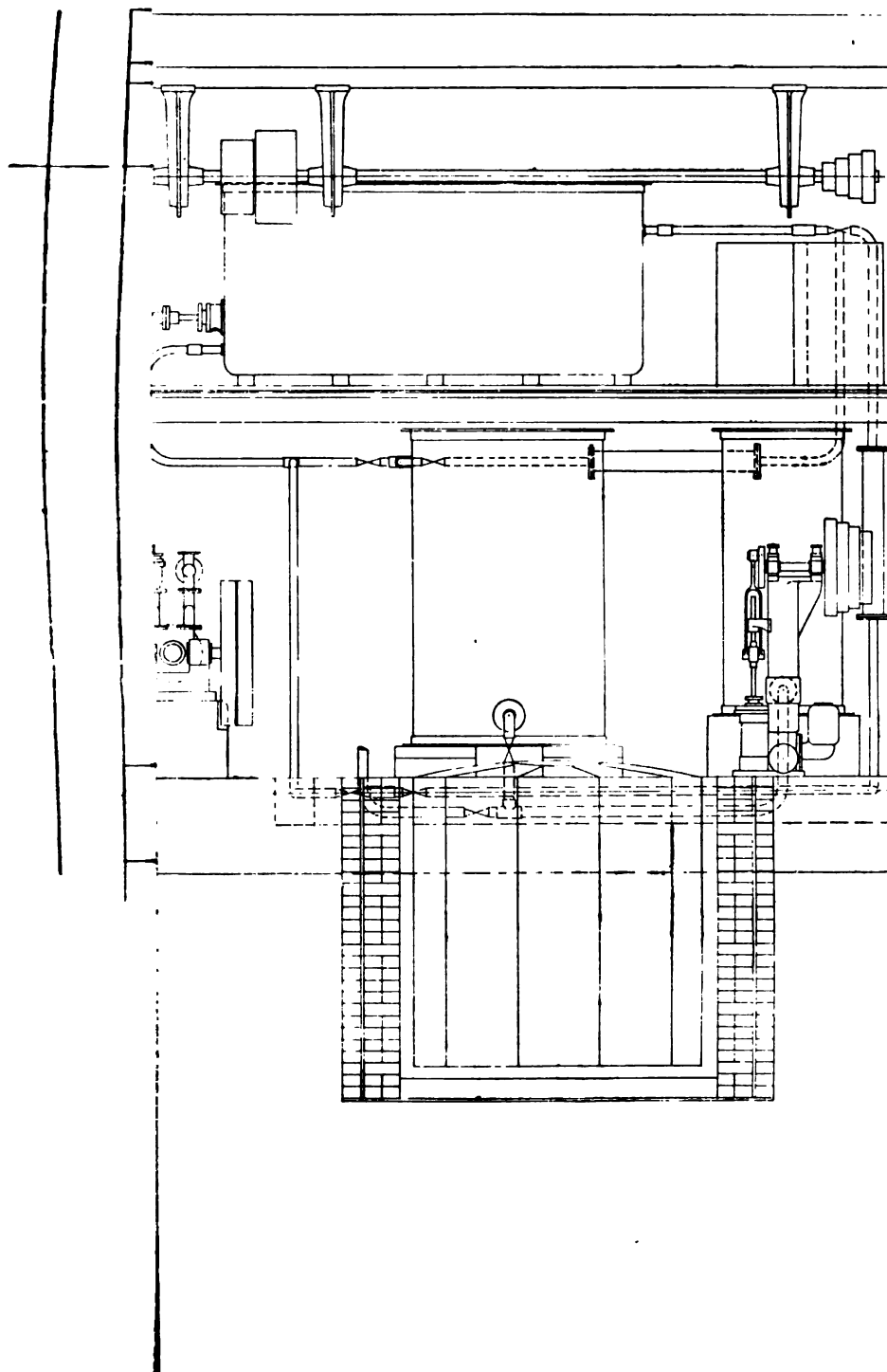
Low Tension Thermal Cut-outs

By Prof. A. SCHWARTZ, m.i.e.e.,
and W. H. N. JAMES, assoc.i.e.e.

THE Thermal Cut-out or fuse is essentially a protective device its function being to guard circuits and apparatus connected therewith from injury due to abnormally large currents. An excess current in a circuit may occasion injury in two ways by setting up : (1) excessive heating; (2) mechanical or electrical strains and effects, either in the conductors themselves or in the apparatus connected to them. In the first case the time duration of the excessive current directly affects the resulting injury, whereas in the second case the damage done may be practically instantaneous. All electrical apparatus should be capable of carrying continuously its normal current without injury, and also of carrying currents considerably in excess of this for short intervals of time. The requirements for an efficient protective device would, therefore, seem to be :—

1. Safe operation with a definite excess current within a given time, at the voltage of the circuit on which it is employed.
2. Efficient operation with currents largely in excess of that required to bring it into action.
3. Suppression of the arc consequent on rupture without explosion or damage to neighbouring parts or connections.
4. Reliability of action.
5. Ease of replacement and inspection.
6. Non-interchangeability of devices of different ranges.
7. Simplicity of construction.
8. Low first cost, and cheap renewal of wire.

In spite of the fact that a vast amount of opprobrium has been heaped upon the thermal cut-out, there seems to be no valid reason why it should not, under proper conditions, fulfil the foregoing requirements. Although fuses have for the last quarter of a century played so important a part in electrical engineering work, no paper dealing directly with them has been presented to this Institution since Cockburn's paper on safety fuses in 1887; it may, therefore, not be out of place to review very briefly their history and development. The fuse for the protection of electric light and power
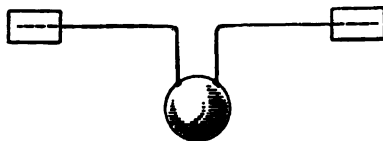
Fig. 1.

circuits is a development of the platinum wire cut-outs in use nearly half a century ago for the protection of submarine cables from the effects of atmospheric electricity. Fuses of various kinds were in use as far back as 1874, and in 1879 Professor S. P. Thompson invented an "improved form of cut-out," shown in Fig. 1. This
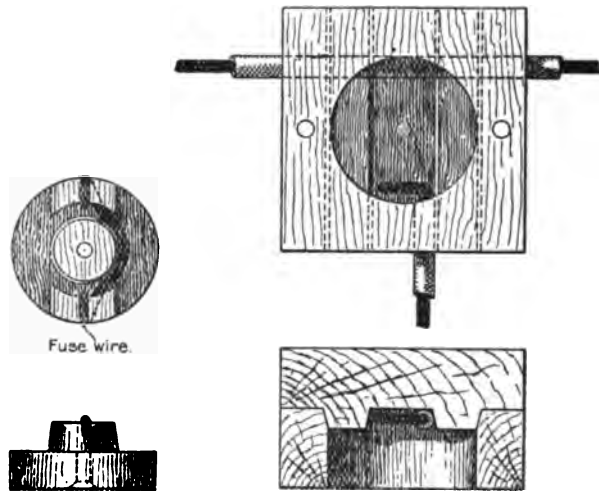
Fuse wire.

Fig. 2.

consisted of two iron wires connected by means of a ball of lead, the wires and ball became heated, and the lead melted, allowing the wires to fly apart. The earliest form of Edison plug fuse dates from 1880. A safety fuse with springs was the subject of a patent by
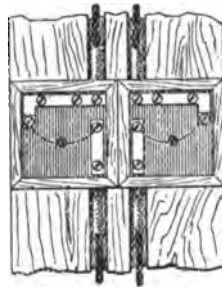
Fig. 3.

C. V. Boys and H. H. Cunynghame early in 1883, and nearly a year later Lord Kelvin produced a somewhat similar form. It consisted of

two pieces of springy copper united by a soldering of fusible metal, which melted at a moderate temperature. Public attention was first directed to the danger of electrical fires by Mr. Musgrave Heaphy in a letter to the *Times* in 1883. The current opinion of electrical engineers was that fuses would introduce into the circuit a greater fire risk than that which they were intended to obviate, and as wood was the prevailing material in use for fuse blocks at that time, they were probably right. A fuse block belonging to this period is shown in Fig. 2. In 1887 Cockburn brought out his well-known weighted fuse, Fig. 3, and the mica foil fuses of Killingworth Hedges were also used successfully. The mounting of fuses on incombustible bases, and their grouping in accessible positions, has led up to the present distributing board system. Progress in America and on the Continent followed somewhat on the same lines; in the States, however, considerable attention has been paid to the development of enclosed fuses of the Mordey pattern with filled tubes; while in Germany the Edison plug type has been largely adhered to, from which the "Patrone," or cartridge pattern, has been evolved. In this country low-tension thermal cut-outs have been developed in three distinct types, each with special features designed to meet the requirements of the service for which it is intended. In central station work and heavy current work generally the fuse has been displaced by the circuit breaker. The three types of circuit in which fuses are employed are given below, together with the general order of magnitude of the currents to be dealt with.

Type of Service.	Current strength per fuse.
1. Distributor boards	3 to 30 amperes
2. House service and switchboards	10 to 100 "
3. Motor services and section pillars on distributing mains	50 to 500 "

Before dealing in detail with the individual requirements of these types, it will be well to consider the behaviour of the wire itself when subjected to currents of fusing strength. The current required to fuse a wire of circular cross-section of given material is dependent upon the following variables :—

     1. Diameter.
     2. Time of current flow.
     3. Length of fuse wire employed.
     4. Environment and position of fuse.
     5. Previous history of fuse wire.

It will be seen from the foregoing that there may be an infinite number of fusing currents for any particular wire. The "normal fusing current" for a given wire, the length and environment of which are constant, may be defined as : The minimum current

required to fuse the wire in such a time interval as shall be necessary for the wire to have attained its maximum steady temperature. The "normal carrying capacity" or "rating" of a fuse wire may be
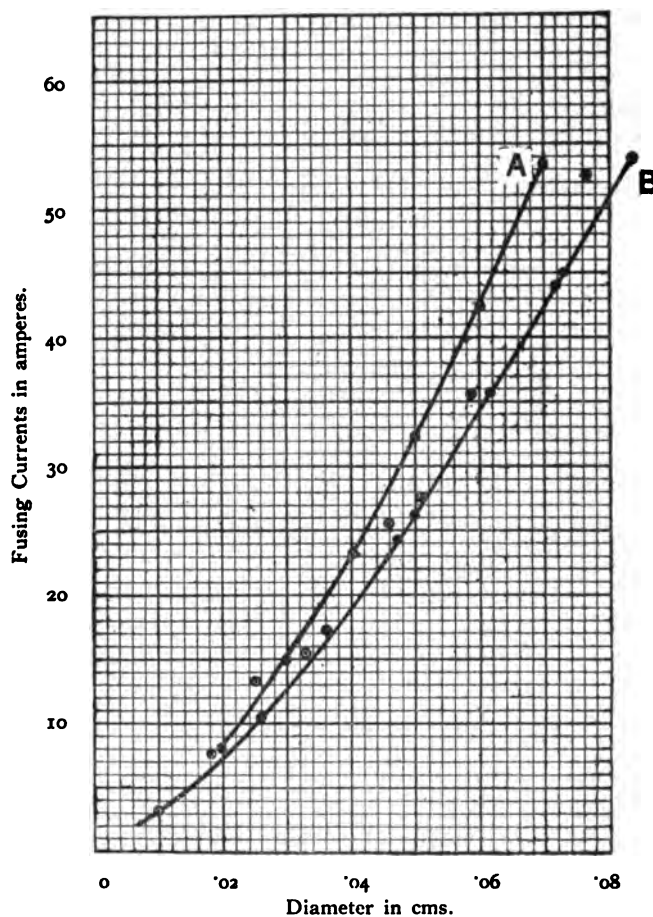
Fig. 4.—Curves connecting Fusing Current and Diameter for Copper Wires.

A. Calculated from Preece's Formula $C = 2887d^{1.5}$.

B. Authors' Experimental Results for Copper and Tinned Copper.

Preece's experimental results for copper shown by points in circles.

defined as: The maximum current which the fuse is capable of carrying continuously without deterioration or undue heating. It

should, in the authors' view, be taken as one half of the normal fusing current for tinned copper wires.

RELATION BETWEEN FUSING CURRENT AND DIAMETER.

The first series of experiments undertaken by the authors was for the purpose of determining whether a law of the character $C = A d^b$ connecting the fusing current (C) and the diameter (d) was
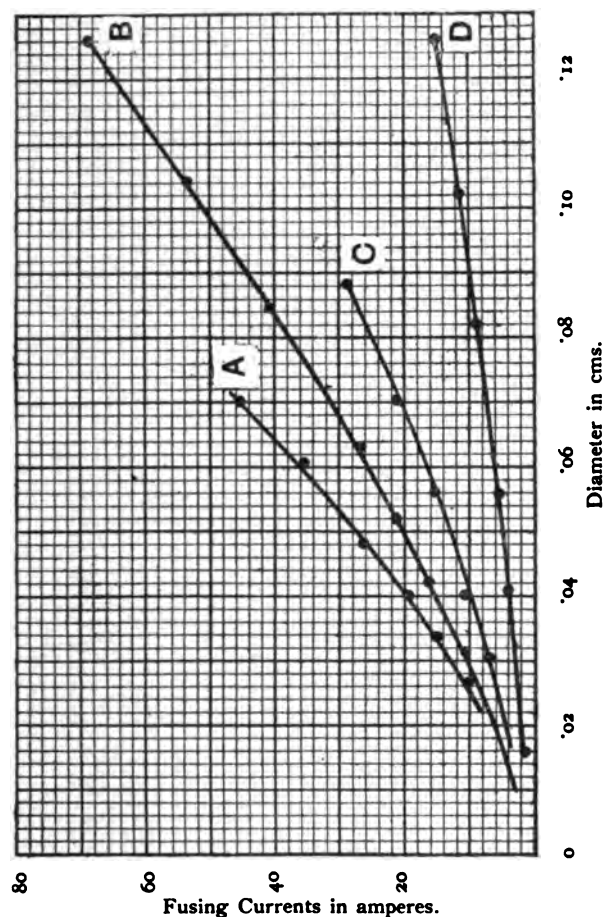
Fig. 5.—Curves connecting Fusing Current and Diameter.

A. Aluminium.   C. Aluminium with Spring attachment.
B. Silver.   D. Tin.

Diameter in cms.

Fusing Currents in amperes.

true over any considerable range. In these experiments commercial tinned copper wires, fusing with currents from 1 to 100 amperes, were employed. The wires were supported horizontally, and were of

such lengths that the fusing currents were independent of the cooling effect of the terminals. In each case the current was increased slowly, and the wire allowed to reach a steady temperature before rupture took place. Curve A, Fig. 4, shows the relation between diameter and fusing current, plotted from Preece's formula $C = Ad^{\frac{3}{2}}$, while the circles mark the actual points which he obtained by experiment.
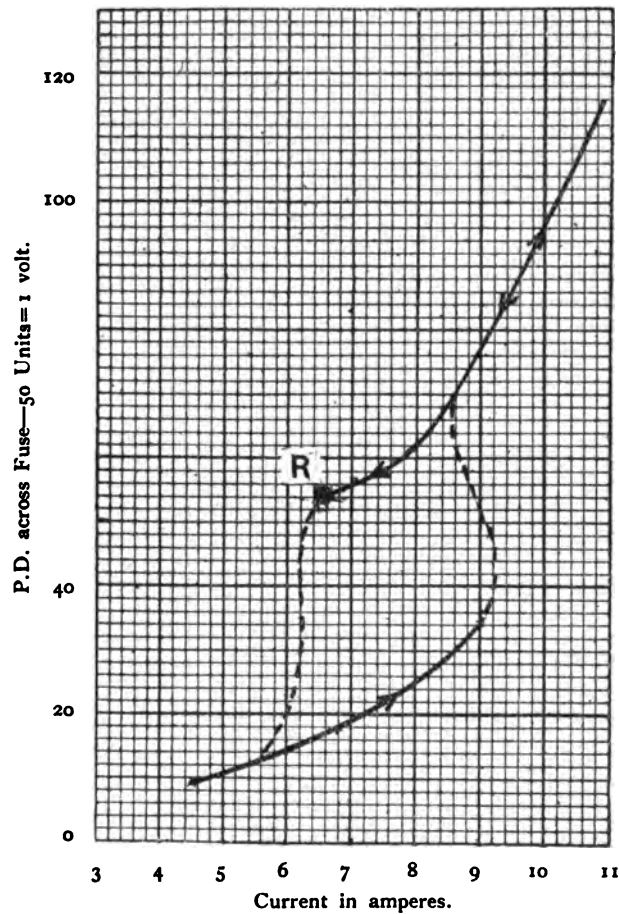
Fig. 6.—Curve showing the behaviour of an aluminium wire with a normal fusing current of 16·9 amperes, in which the current has been raised to 11 amperes and then gradually reduced ; the wire rupturing at the point marked R as the current was being reduced.

Preece's re-determination of the constant for copper in 1890 gives a curve which lies intermediate between A and B, and coincides very nearly with his experimental results. Curve B, Fig. 4, shows the authors' results for tinned copper and pure copper. It is noticeable that the values for pure copper and tinned copper are practically coincident; this is due to the small quantity of tin employed in the coating. The curves in Fig. 5 show the relation between diameter and fusing current for wires of silver, tin, and aluminium. In common with wires of lead and tin and their alloys, aluminium wires, particularly in the smaller diameters, are considerably affected as to their fusing current by the action of the atmosphere. A layer or skin of oxide or carbonate is formed of sufficient thickness and strength to hold up the metallic core of the wire when in a molten condition. Such wires break by the molten metal draining from the upper to the lower portion of the wire; the fusing current is consequently abnormal. This defect was noticed by Cockburn in connection with tin fuses, and he loaded his wires at the centre with a small lead ball to ensure prompt rupture. With aluminium wire this skin is particularly tough, and has a large effect upon the fusing current. This is shown in curves A and C, Fig. 5. Curve A is for aluminium wire, held in the ordinary way between terminals. Curve C shows the results obtained when the wire was placed under tension by means of a weak spring attached to one of the terminals. The same results may be obtained by making use of the repelling action of a magnet in place of the spring attachment. If an aluminium wire, supported between terminals in the ordinary way, be subjected to a current sufficient to produce the fusion of the wire but not its rupture, and the current be then gradually reduced, the metal will remain molten even with quite a small percentage of the current originally necessary to produce fusion. This is due to the increased resistance offered by the molten metal and the greater quantity of heat produced in the fuse in consequence. As the resistance of the fuse compared with that of the whole circuit is negligible, the current flow will be the same in both cases. It is, in fact, rather a difficult matter to cause the metal to solidify again, as the fuse often ruptures as the current is being reduced. If, however, the metal solidifies without the rupture of the wire taking place, and the current be again raised to the point of fusion, the curve first obtained is nearly reproduced. The experimental results illustrating this point are shown graphically in Fig. 6. In the case of fuses enclosed in tubes packed with sand, chalk, asbestos or other incombustible material, this effect is naturally intensified as the molten wire is closely supported on all sides, and special means have to be adopted to overcome the difficulty thus introduced. Curves B, C, D and E, Fig. 7, show the relation between Log. d (diameter) and Log. C

(fusing current) for various metals, the spring attachment being used in the case of aluminium. Curve A shows the slope corresponding to Preece's Index of 1·5. It is evident that this slope does
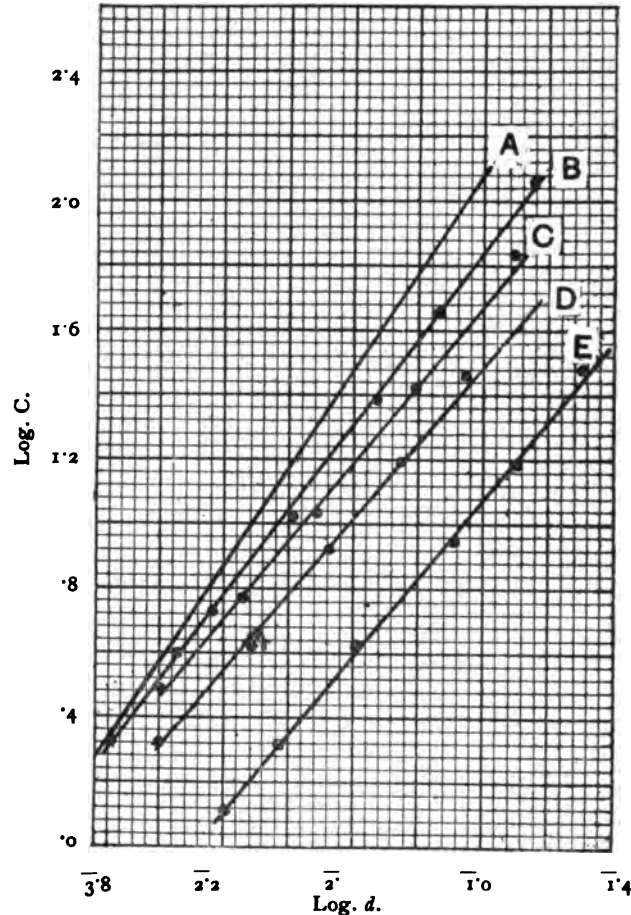
Fig. 7.—Curves showing relation between Log. *d* (diameter) and Log. C (fusing current).

A. Slope corresponding to Preece's Index, 1·5.
B. Copper.
C. Silver.
D. Aluminium (critical current).
E. Tin.

not fit the curves of experimental results. An examination of the observed points on the curves B, C, D and E shows that a law of the order $C = Ad^b$ does not hold over the whole range. For small diameters the points lie above the line, while for the intermediate values they lie below the line, rising above the line again for the higher values. Preece states that his law gives values for C which are too low for small diameters, but we find that his values are also too high for the larger diameters. Determining the law for tinned copper over a large range (1 to 100 amperes), curve B, Fig. 7, the best values of A and b are contained in the formula

$$C = 1435 d^{1\cdot 297} \quad (d \text{ in cms.}).$$

The above law gives somewhat low values for wires of large diameters. The current range from 1 to 100 amperes was therefore divided into two parts, 1 to 10 amperes and 10 to 100 amperes, and the best law found for each case, with the following results :—

Range 1 to 10 amperes $C = 821\cdot 3 d^{1\cdot 195}$.

" 10 to 100 " $C = 1768 d^{1\cdot 403}$.

d = diameter of wire in centimetres.

Tables I. and II. show the agreement between the values for the fusing currents for tinned copper wires of various diameters as calculated from the above laws, and the actual fusing currents for these wires as found by experiment.

TABLE I.

For tinned copper wires for fusing currents between 1 and 10 amperes.

Diameter in cms.	Fusing current calculated from $C = 821\cdot 3 d^{1\cdot 195}$	Observed fusing current.
·0049	1·43 amps.	1·5 amps.
·0117	4·04 „	4·0 „
·0151	5·48 „	5·5 „
·026	10·5 „	10·6 „

TABLE II.

For tinned copper wires with fusing currents between 10 and 100 amperes.

Diameter in cms.	Fusing current calculated from $C = 1768 d^{1\cdot 403}$.	Observed fusing current.
·026	10·54 amps.	10·6 amps.
·0474	24·5 „	24·4 „
·0834	54·1 „	54·0 „
·144	116·5 „	115·0 „

It will be seen from these tables that the calculated and observed values are practically in agreement. For diameters in inches the law is expressed as follows for horizontal wires :—

Range 1—10 amperes $C = 2501 d^{1\cdot 195}$.

" 10—100 " $C = 6537 d^{1\cdot 403}$.

The values of the index and constant necessary for use with various metals with the diameters in inches, centimetres and millimetres for wires in vertical or horizontal positions with large and small terminals, and for certain standard lengths, are given in tabular
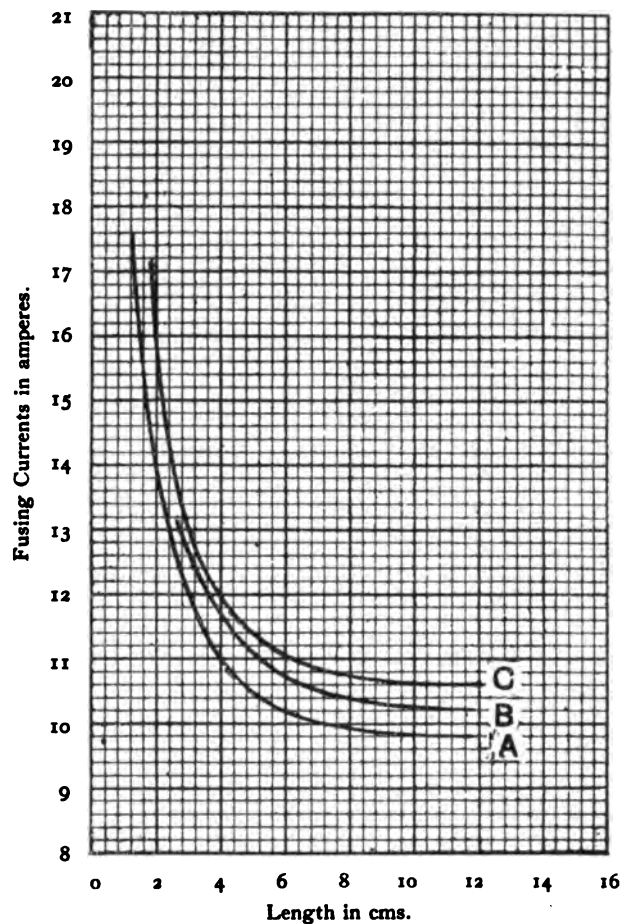
Fig. 8.—Curves showing effect of position on Fusing Current of a tinned copper wire No. 33 S.W.G., normal fusing current 10·6 amperes.

A. Vertical.
B. Inclined at 45°.
C. Horizontal.

form in the Appendix. For silver wires over the whole range given
(1 to 70 amperes)

$$C = 3210d^{1\cdot 287} \ (d \text{ in inches}).$$

It is again evident from the curve B, Fig. 5, that a law of the above
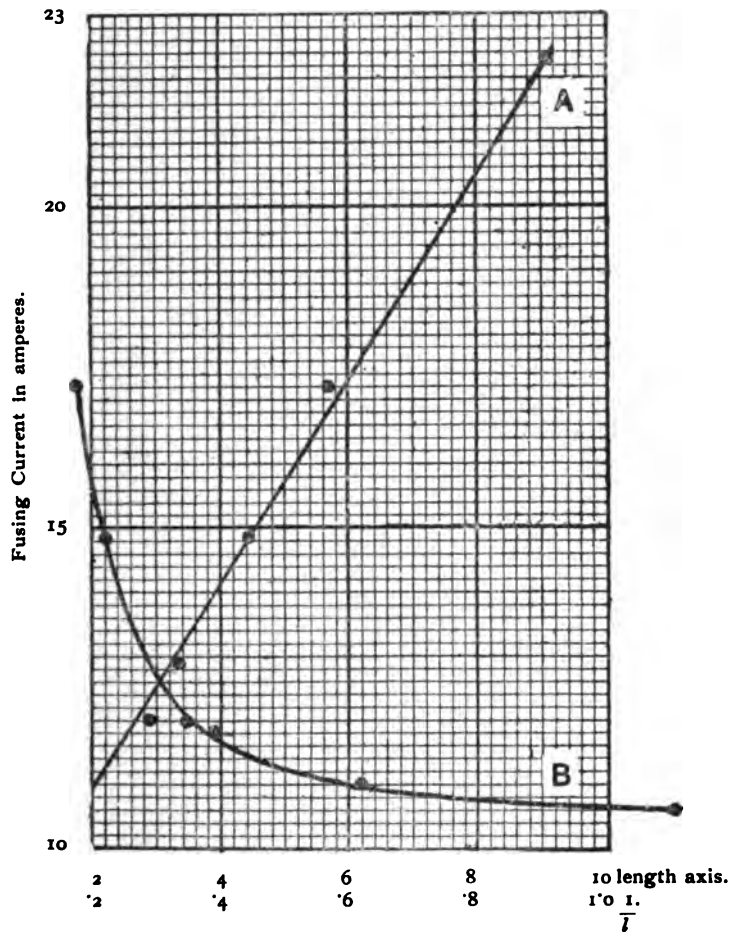
Fig. 9.—Curves for a Tinned Copper Wire, No. 33 S.W.G. horizontal.

Curve A shows the relation between $\dfrac{1}{l}$ and fusing current.

Curve B shows the relation between l and fusing current.

form is not strictly true over the whole range, and if more accurate results are desired the curve must be subdivided. For aluminium wires and fusing currents up to 50 amperes

$$C = 8539 d^{1.461} \quad (d \text{ in inches}).$$
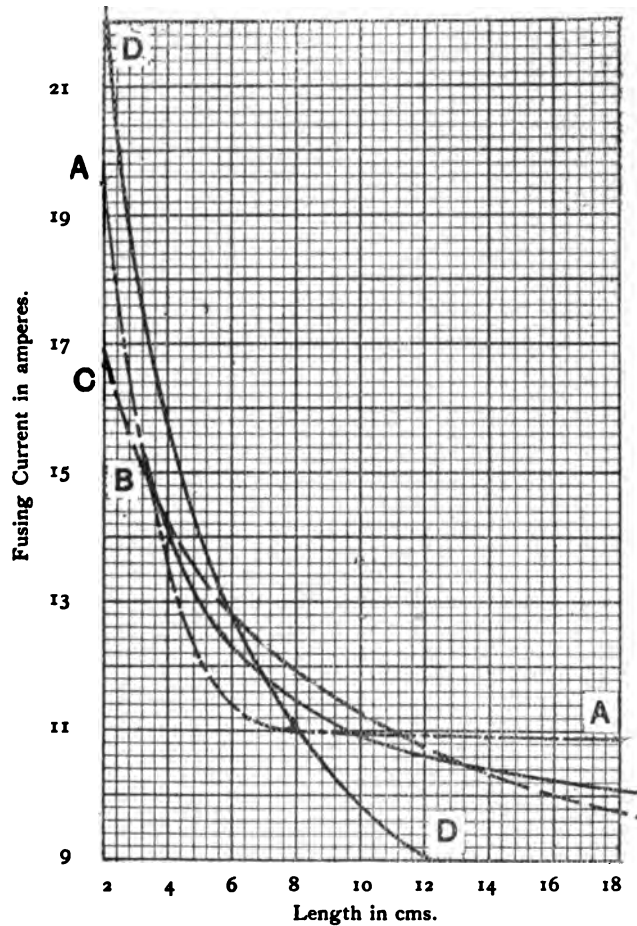
Fig. 10.—Curves showing the relation between Fusing Current and length for a lead wire 1 mm. diameter.

A. Grassot's Experimental Results.
B. Calculated from Authors' Formula.
C.   „   „   Grassot's Formula.
D.   „   „   Skrschinski's Formula.

This approximates to the index for aluminium obtained by Preece, but the circumstances are not quite normal, since at about 50 per cent. of the ultimate fusing current the metal becomes molten in the core of the wire, and rupture finally takes place as already pointed out, due to the draining of the metal to the lowest point of the fuse.
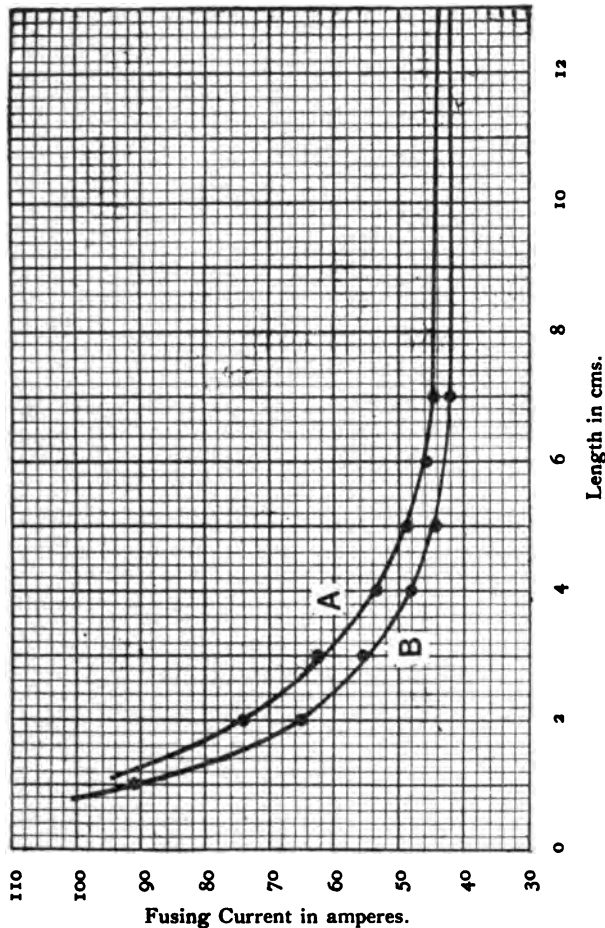
Fig. 11.—Curves showing the effect of mass of terminals on a lead wire, No. 13 S.W.G., with a normal fusing current for a length independent of the mass of the terminals of 42 amperes.

A. Large terminals weighing 870 grms. each.
B. Small " " " 18 " "

The law connecting the diameter with the critical current for aluminium wires, that is the current at which the metal becomes

molten is $C = 2091d^{1.371}$ (d in inches). For tin wires the law again does not hold over the whole range :—

$$\left.\begin{array}{llll}\text{Range} & 1\text{—}10 \text{ amperes} & C = 420 \cdot 6d^{1.131} \\ \text{\textit{„}} & 10\text{—}80 & \text{\textit{„}} & C = 819d^{1.83}\end{array}\right\}d \text{ in inches.}$$

<div style="text-align:center">EFFECT OF POSITION.</div>

For copper wires the effect of being in a vertical position instead of a horizontal one is to decrease the fusing current by about 6 per cent. for wires of small diameter with fusing currents up to 10 amperes. This is best expressed in the formula by keeping the index constant and altering the constant. For lengths of $1\frac{1}{4}$ inches with small terminals

$$C = 3611d^{1.264} \text{ (d in inches)}.$$

as against a constant $= 3828$ when horizontal. For larger wires, with fusing currents, from 10 to 100 amperes, the decrease in fusing current when vertical instead of horizontal is about five per cent. with lengths of four inches and large terminals. The change in the constant is as follows :—

$$\left.\begin{array}{ll}\text{Vertical} & C = 12470d^{1.586} \\ \text{Horizontal} & C = 13100d^{1.586}\end{array}\right\}d \text{ in inches.}$$

Fig. 8 gives curves connecting fusing current and length for a tinned copper wire A vertical, B at 45°, C horizontal. The effect of shortening the length of the fuse wire is to increase the index and the constant. Tinned copper wires with fusing currents up to 10 amperes and small terminals in lengths of two inches and upwards have the same fusing current as for long lengths. For lengths below two inches the index and constant are increased as follows :—

$$\begin{array}{lll}\text{Length.} \\ 1\frac{1}{2}\text{in.} & C = 3611d^{1.26} \\ 1 \text{ in.} & C = 5060d^{1.32}\end{array} \left\{\begin{array}{l}d \text{ in inches.} \\ \text{wires vertical.} \\ \text{small terminals.}\end{array}\right.$$

$$\begin{array}{lll}1\frac{1}{2}\text{in.} & C = 5890d^{1.34}\end{array} \left\{\begin{array}{l}d \text{ in inches.} \\ \text{wires vertical.} \\ \text{large terminals.}\end{array}\right.$$

$$\begin{array}{lll}1\frac{1}{2}\text{in.} & C = 3828d^{1.264} \\ 1 \text{ in.} & C = 5360d^{1.32}\end{array} \left\{\begin{array}{l}d \text{ in inches.} \\ \text{wires horizontal.} \\ \text{small terminals.}\end{array}\right.$$

<div style="text-align:center">RELATION BETWEEN FUSING CURRENT AND LENGTH.</div>

A number of experiments were made with tinned copper wires to determine the relation between fusing current (c) and length (l), and on plotting fusing currents as ordinates and $\frac{1}{l}$ as abscissæ, a straight

line over a considerable range was obtained—see Fig. 9, curve A. This corresponds to a law of the form $C_l = M + \dfrac{N}{l}$, where M and N are constants depending on the diameter and "l" is the length of wire employed. It was found that $M = P\, C_n$

$$\text{and } N = Qd^2;$$

where P and Q are constants for a given material with terminals of a definite mass and independent of the diameter of the wire.

$C_n =$ normal fusing current for wires sufficiently long to be independent of the cooling effect of the terminals.

$C_l =$ fusing current for a wire of length "l" cms.

$d =$ diameter.

For tinned copper wires the experimental determinations of these constants are shown in Table III., while for lead wire Grassot's* experimental results have been taken and collated in Table IV.

TABLE III.

Authors' Experimental Values for Constants P and Q for Tinned Copper Wires.

d Diameter in cms.	M	N	C_n Amperes.	$P = \dfrac{M}{C_n}$	$Q = \dfrac{N}{d^2}$
·0049	1·31	0·52	1·5	·173	21,660
·007	1·87	0·94	2·1	·890	19,180
·0117	3·5	2·4	·0	·875	17,540
·0149	4·69	4·31	5·35	·876	19,410
·0151	4·53	4·52	5·5	·824	19,820
·0260	9·2	12·4	10·6	·868	18,340
·0474	20·3	43	24·4	·832	19,140
·062	31·5	65	36	·875	16,910

From the above table the mean values for tinned copper are as follows, P = ·864, Q = 19,000, so that the fusing current C_l for a length of "l" centimetres of tinned copper wire may be obtained from the formula—

$$C_l = ·864 C_n + \frac{19,000 d^2}{l}$$

C_n being the normal fusing current as previously defined.

TABLE IV.

Values of Constants P and Q from Grassot's Experimental Results for Lead Wire.

d Diameter in cms.	M	N	C_n Amperes	$P = \dfrac{M}{C_n}$	$Q = \dfrac{N}{d^2}$
·05	3·23	5·55	4·0	·807	2,220
·055	3·74	6·92	4·6	·813	2,288
·07	5·97	9·07	7·0	·853	1,851
·085	7.22	14·56	8·9	·811	2,015
·09	7·74	16·52	9·9	·782	2,039

* Grassot, *l'Electricien*, vol. 10, p. 419, 1886.

From the above table the mean values of the constants for lead wire are as follows :—

$$P = \cdot 813. \qquad Q = 2083.$$

So that for lead—

$$C_l = \cdot 813 C_n + \frac{2083\,d^2}{l}$$

l = length in cms.

It is a difficult matter to obtain an exact expression for the relationship between the fusing current and length of a wire. Skrschinski,[*] as the result of his experiments on lead wire of diameters from 0·62 to 1·55 mm. gives $C^2 l = K d^3$; Feldmann,[†] from considerations of the experimental results of Reinisch[‡] and Grassot,[§] gives $C^2 \sqrt{l} = A d^3$.

The mean values for the constants of these investigators are as follows :—

Skrschinski $C^2 l = (9 \cdot 96)^4 d^3$
Grassot $C^2 \sqrt{l} = 1267 d^3$
Reinisch $C^2 \sqrt{l} = 1906 d^3$

Feldmann :—

(1) For terminals weighing 300 grms. $C^2 \sqrt{l} = 1350 d^3$
(2) For terminals weighing 60 grms. $C^2 \sqrt{l} = 1000 d^3$ ·
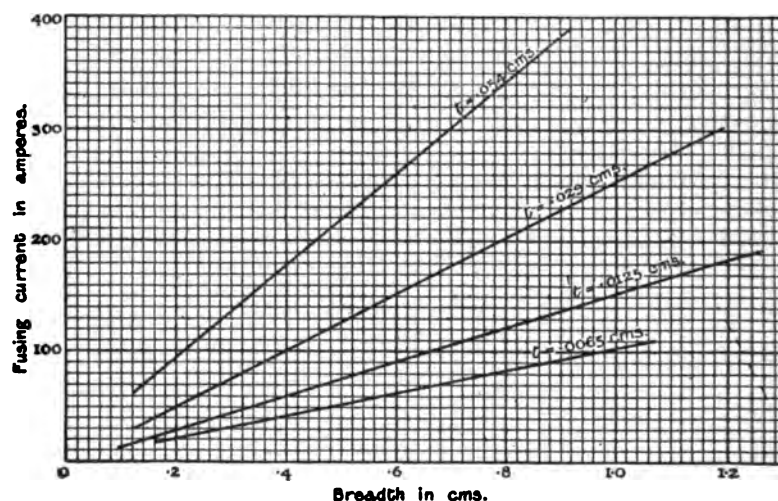
Fig. 12.—Curves connecting Fusing Current and breadth for copper strips of constant thickness t. Strips horizontal length 5¼ inches. Terminals weighing 49 grms. each.

* No. 3 des Elektritschestwo, Dec. 14, 1890.
† Ueber Bleisicherung, Elektrotechnische Zeitschrift, vol. 13, 1892.
‡ Zeitschrift für Elektrotechnik, vol. 1, p. 243.
§ l'Electricien, vol. 10, p. 419, 1886.

Feldmann was the first to show the influence which the mass of the terminals has on the fusing current. In order to obtain a direct comparison between the results given by the authors' law $C = M + \dfrac{N}{l}$ and the laws $C^2 l = k d^3$ and $C^2 \sqrt{l} = A d^3$ enunciated by the above-named investigators, Grassot's experimental results have been taken as a basis. These experimental results are shown in Fig. 10, curve A; the calculated results from the authors' law are shown in curve B, from Skrschinski's law, curve D, and from Grassot's law, curve C. In the case of curve D, Skrschinski's
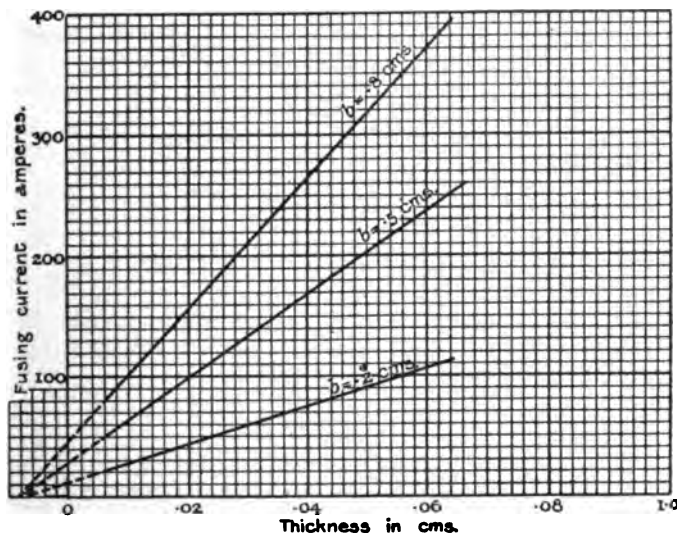
Fig. 13.—Curves connecting Fusing Current and thickness for copper strips of constant breadth; "b" strips horizontal length 5½ inches. Terminals weighing 49 grms.

constant was used; this holds true only for the terminals he employed. Their mass is not stated, but they were probably very heavy.

EFFECT OF TERMINALS.

The effect of the length of wire employed and the mass of the terminals is much greater in the case of lead than in the case of copper, owing to the increased cross-sectional area required for a given current-carrying capacity. The radiating surface being directly proportional to "d," while the surface available for the conduction of heat along the wire is proportional to d^2. Fig. 11

shows the cooling effects due to using terminals of different mass; curve A shows the relation between fusing current and length for a lead wire with a normal fusing of 42 amperes, the wire being supported horizontally and the mass of the terminals being 870 grms. each. Curve B shows similar results with smaller terminals weighing 18 grms. each. For copper wires this effect is very much smaller; in fact, with copper wires with fusing currents up to 10 amperes and lengths of 2 inches and upwards it may be neglected. Experiments with small terminals weighing 4 grms. taken from a commercial form of fuse holder gave the following results :—

TABLE V.

Effect of Terminals of Clipholder for Distribution Board on Tinned Copper Wires. Wires, horizontal; length, 2in.

Diameter in cms.	Fusing current for lengths independent of cooling effect of terminals.	Fusing current in commercial holder. Length, 2in.
·0049	1·5	1·5
·007	2·1	2·15
·0117	4·0	4·02
·0151	5·5	5·47
·026	10·6	10·9

The general form of the curves obtained from the authors' experiments on the effect of terminals of different mass is in agreement with the results obtained by Feldmann.

COPPER STRIP.

With copper strip the fusing current is proportional to the breadth with a constant thickness. The experimental results showing this are given in Fig. 12. It will be noticed that these curves practically all pass through the origin. If, however, we plot thickness against fusing current for strips of constant breadth, Fig. 13, we see that the curves pass through a point on the axis of thickness considerably to the left of the origin; this is probably due to the increased carrying capacity per unit area in the small strips owing to their relatively greater cooling surface. In Fig. 13 the full lines show the portions of the curves actually obtained by experiment, the dotted lines show these curves produced; the actual experimental curves if carried down to very low values would pass through the origin. It is probable that experiments with copper strip of greater thicknesses than those the authors have employed would show that the relation between breadth and thickness was not represented over the whole range by a straight line, but by a curve. A consideration of the curves in Figs. 12 and 13 shows that a law of the character

$$C = Ab \ (t+k) \text{ obtains;}$$
$$\text{where } C = \text{fusing current,}$$
$$b = \text{breadth,}$$
$$t = \text{thickness.}$$

With a length of $5\frac{1}{4}$ inches and the breadth and thickness in inches,

$$C = 40,550 \ b \ (t + \cdot 00355).$$

In centimetre measure

$$C = 6,280 \ b \ (t + \cdot 009).$$

The effect of length on the constant can be most easily expressed in the form of curves. Fig. 14 shows the relationship between the length in inches, and the constant "A," the constant "k"—which is necessary on account of the curves not passing through the origin as already mentioned—remaining constant. Curve A is for a vertical position, and curve B for a horizontal position of the strips. It will
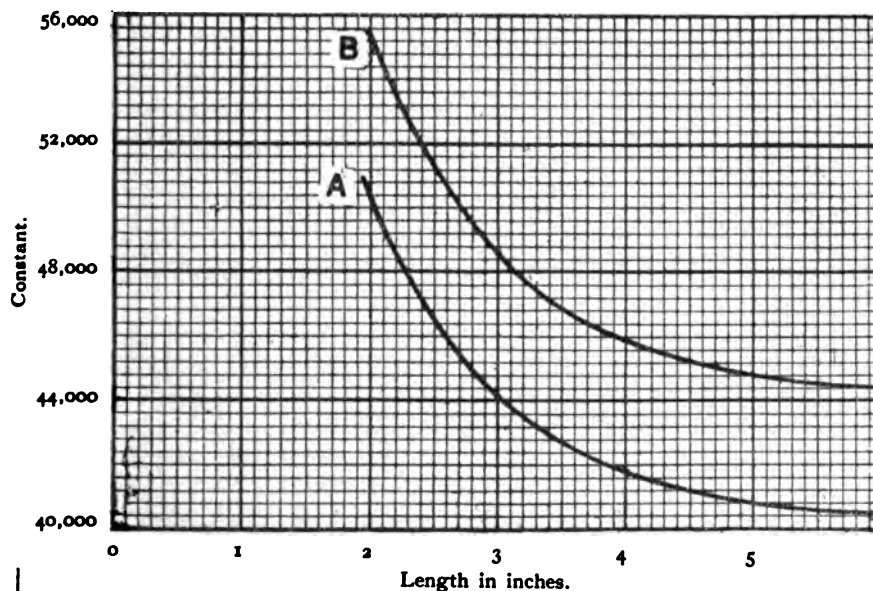
Fig. 14.—Curves connecting the Constant "A" in the formula.
$C = Ab(t+k)$ for copper strip.
Curve A. Strip vertical.
Curve B. Strip horizontal.

be noticed that the effect of position is more marked in the case of strips than in the case of wires. The decrease in fusing current due to a vertical position *vice* a horizontal position being about 10 per

cent. for strips as against 6 per cent. for wires. Table VI. shows the agreement between the observed fusing current for copper strip in a horizontal position and the values calculated from the authors' formula.

TABLE VI.

Observed Values for Fusing Current in Horizontal Copper Strips and Values calculated from the Authors' formula $C = 6920b\ (t + \cdot009)$.

Thickness in cms.	Breadth in cms.	Calculated fusing current.	Observed fusing current.
·0055	0·8	80·2	78·8
·0065	0·4	42·8	42
·0125	0·3	44·6	46·8
·029	1·0	262·6	257
·054	0·6	261·2	260·5

LEAD STRIP.

The curves connecting fusing current and breadth for lead strip are similar in character to those given for copper, and are therefore not shown. There is this difference, however, that when extended backwards they do not pass through the origin, but cut the axis of breadth at a point to the left of it. This is due to the higher current density in the narrow strips. This effect is much more marked in the case of lead than in the case of copper. On plotting fusing current against thickness for a constant breadth, a straight line was not obtained; the curve, however, follows a logarithmic law—that is to say, with a constant breadth the fusing current is not proportioned to the thickness "t" but to t^n.

For lead strips $n = \cdot74$. The fusing current for vertical lead strips is given by the following equation :—

$$C = 2060\ t^{\cdot74}\ (b + \cdot016).$$
$$\text{``}b\text{'' and ``}t\text{'' in inches.}$$

The range of experiments from which this law was deduced was as follows :—Thickness 0·0005 inch to 0·055 inch.

Breadth 0·08 inch to 0·4 inch.

Fusing currents 4 amperes to 100 amperes.

This formula can be relied on to within 3 per cent. with good commercial lead. An analysis of the sample used gave 99·8 per cent. of lead. The agreement between the calculated and observed values for the fusing current of lead strip is shown in Table VIa.

TABLE VIa.

Observed Values for the Fusing Current of Vertical Lead Strip and Values calculated from the Authors' formula $C = 407t^{\cdot74}\ (b + \cdot04)$.

Breadth in cms.	Thickness in cms.	Calculated fusing current.	Observed fusing current.
·46	·022	12·1	11·8
·96	·141	95·5	95·4
·75	·141	75·4	75·0

EFFECT OF ENCLOSURE IN TUBES.

A series of experiments was carried out with a No. 33 S.W.G. tinned copper wire, free in air from terminal to terminal. The wire was placed along the axis of the tube, which extended the whole length of the wire, the ends of the tubes being left open. Tubes of glass
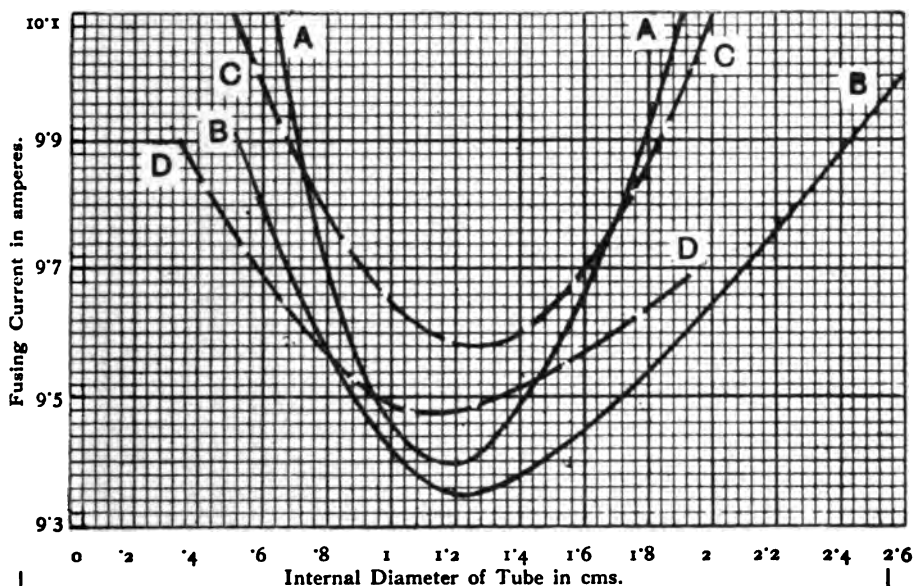
Fig. 14A.—Curves showing relation between the Fusing Current of No. 33 S.W.G. tinned copper wire and the diameter of the tube enclosing it.

A. Brass tubes horizontal.   C. Glass tubes horizontal.
B.   „   vertical.   D.   „   vertical.

Wires placed along axis of tubes free from the sides ; ends of tubes open.
Normal fusing current of the wire in air 10·6 amperes.

and of brass were employed, with internal diameters varying from 0·4 to 2·6 cms., the tubes being arranged vertically and also horizontally. The effect on the fusing current of the wire is shown graphically in Fig. 14a. It will be noticed that in each case there is a certain size of tube for which the fusing current is a minimum, any departure from this size of tube with the size of wire employed producing an increase in the fusing current.

POWER LOSSES IN FUSES.

The power lost in a fuse wire of given length will depend upon :—

1. The normal fusing current; which depends, amongst other things, upon the melting point of the metal employed.

65

2. The strength of the current passing through the wire.
3. The specific resistance of the metal when cold.
4. The coefficient of increase of resistance with temperature.

The rate of increase of the power losses with an increased percentage of the fusing current depends to a large extent upon the last item. This is very noticeable in the case of copper. In Fig. 15 curves are given for tinned copper wire showing the relation between the per-
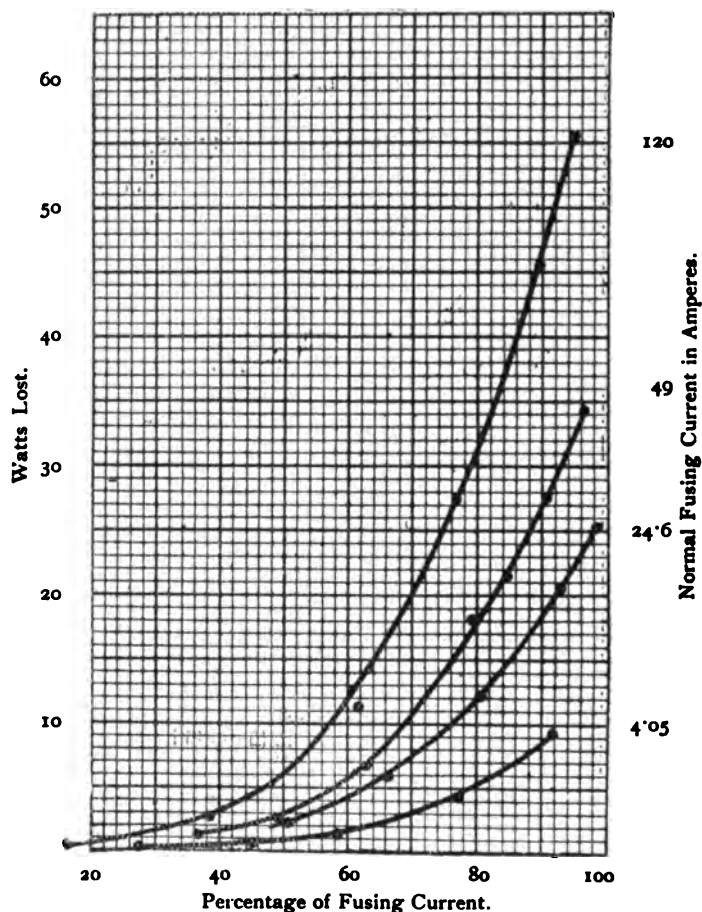
Fig. 15.—Curves showing relationship between watts lost and percentage fusing current for tinned copper wires of various diameters and a length of 8·5 cms.

centage of fusing current in the wire and the watts lost. It will be
seen that up to 50 per cent. of the normal fusing current the losses are
comparatively small, but that above this value the losses increase
very rapidly. This is due to the large temperature coefficient of
copper. Fig. 16 shows a similar set of curves for aluminium wires of
different diameters. The inset on the curve at the point marked A is
due to the sudden increase in resistance on the wire melting within
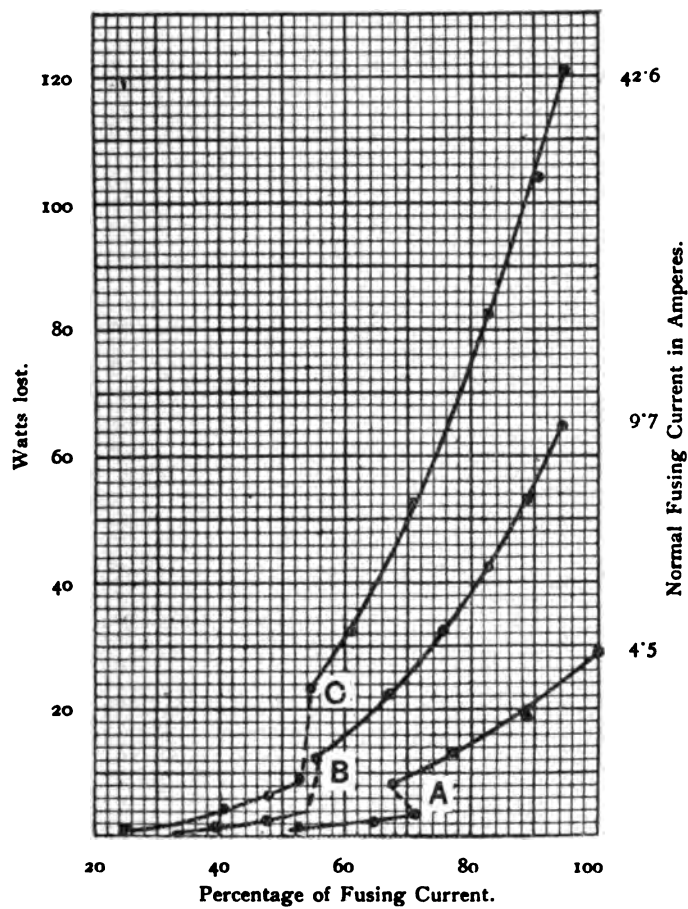
Fig. 16.—Curves showing relation between watts lost and percentage of
fusing current for aluminium wires of various diameters with a length
of 8·5 cms.

its skin of oxide and the consequent diminution of the current, the voltage of the circuit in this case being low and kept constant. At the points B and C this effect is absent, as the external resistance in the circuit was diminished in order to compensate and keep the current strength constant. In these experiments the wire was allowed to remain in a molten condition within the oxide film, and no spring attachment was used. Fig. 17 shows the power lost in tin wires. The smaller wires behave much in the same way as aluminium
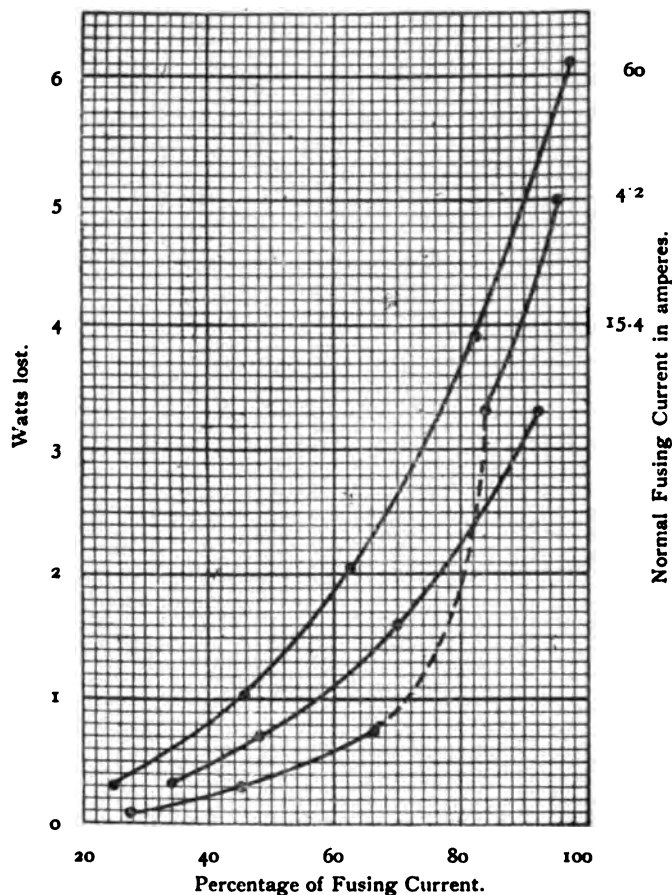
Fig. 17.—Curves showing the relation between watts lost and percentage of fusing current for tin wires of various diameters and a length of 8·5 cms. The dotted line shows the increase in resistance due to the wire fusing inside a skin of oxide.

wires as regards the oxide coating. The wires of larger diameter seem to rupture when the metal becomes molten. The same effect has been observed in the case of aluminium wires of large diameter; it is due to the film of oxide being unable to support the large mass of molten metal. Fig. 18 shows a comparison between the power losses in wires of tinned copper, silver, aluminium, and tin under the same
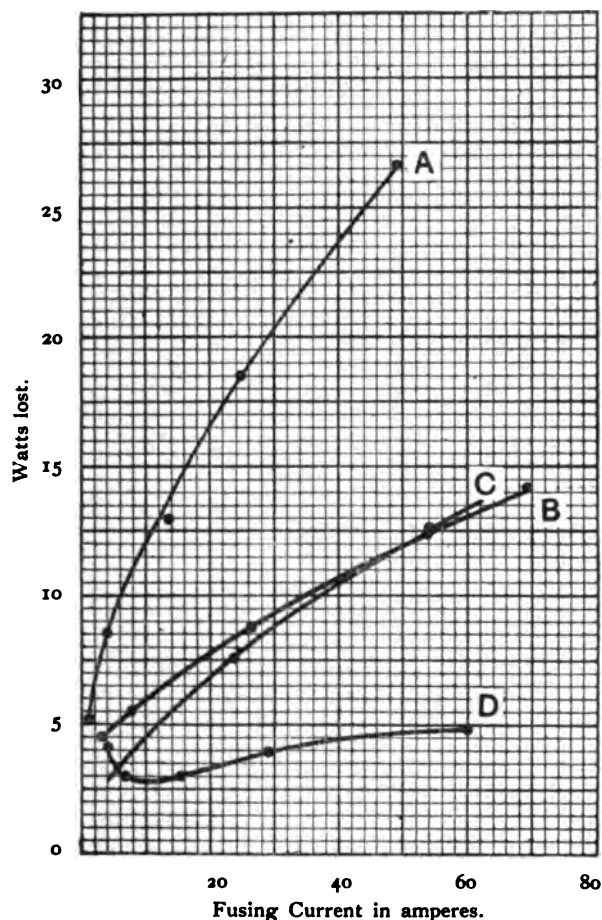
Fig. 18.—Curves showing the relation between the watts lost at 90 per cent of the fusing current and fusing current for wires of different materials with a length of 8·5 cms.

A. Tinned Copper.   C. Aluminium (with spring attachment).
B. Silver.   D. Tin.

conditions. In these curves the fusing currents are plotted as abscissæ, and the watts lost at 90 per cent. of the fusing current as ordinates. Fig. 19 shows a similar set of curves, but in this case the ordinates represent the watts lost at 50 per cent. of the fusing current. In curves A and C the difference in the losses in aluminium
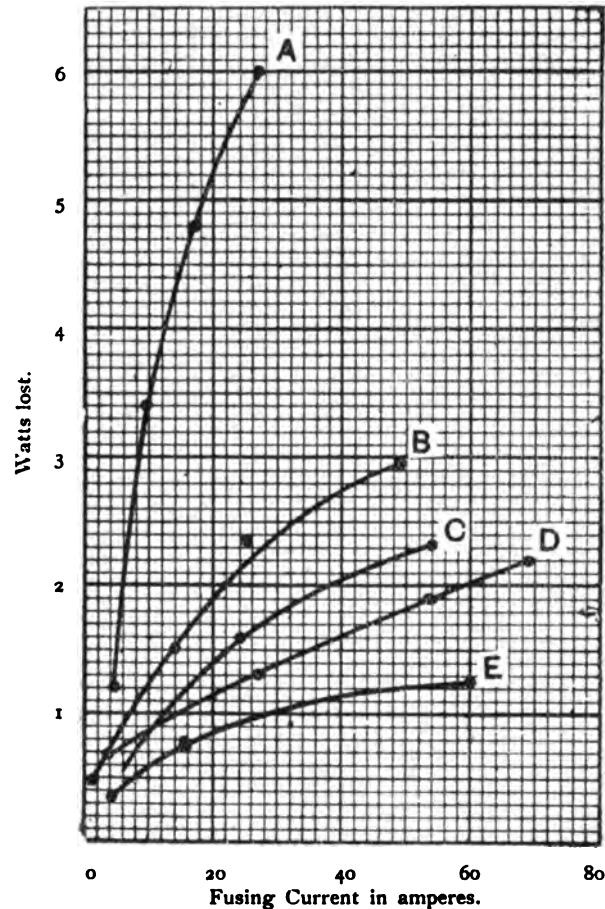
Fig. 19.—Curves showing the relation between the watts lost at 50 per cent of the fusing current and fusing current for wires of different materials with a length of 8·5 cms.

A. Aluminium (no spring).   D. Silver.
B. Tinned Copper.   E. Tin.
C. Aluminium (with spring attachment).

wires with and without the spring attachment is very noticeable. Tin is the most economical metal to use; then come silver, aluminium (with spring attachment), copper, and aluminium (without spring), in the order named. Having regard to the above results, it would seem desirable to run copper fuses at 50 per cent. of their *normal fusing current* rather than at a higher rate. The temperature attained under normal load will then be moderate, and oxidation will be slight. On the other hand, fuses rated to blow with an excess current of 50 per cent. of their *normal carrying capacity* get far too hot, and oxidise to such an extent as to require frequent inspection and renewal. Heim* has made a number of determinations of the drop in fuses in actual installation, with the following results :—

TABLE VII.

A.—Lead Fuses for 110 volts complying with the regulations of the German Institution of Electrical Engineers.

Normal carrying capacity in amperes	30	60	100
Voltage drop per fuse	0·051	0·057	0·061

B.—Small Plug Fuses from the A.E.G. with Silver Wire for pressures up to 250 volts.

Normal carrying capacity in amperes	0·5	1	2	4	6
Voltage drop per fuse	0·12	0·12	0·45	0·12	0·10

C.—Plug Fuses from the A.E.G. for 550 volts with Silver Wire.

Normal carrying capacity in amperes	2	4	6	15	20
Voltage drop per fuse	0·48	0·36	0·26	0·19	0·15

It will be noticed from this table that the voltage drop in these fuses increases with the pressure of the services for which they are intended. This is due to the increased length of fuse required to deal successfully with short circuits at the higher voltages. The authors' experiments on copper fuses show that in general an average drop of 0·15 volt may be reckoned on per fuse way at full load. In an ordinary house installation we may assume that the current for any particular lamp will have to pass through three double-pole fuses on its journey from the supply company's mains to the lamp in question. The total pressure drop in the fuses will therefore be $3 \times 2 \times 0·15 = 0·90$ volt; a drop which should certainly not be neglected when considering the total drop in volts in the circuit. Fuses immersed in oil have a large drop in volts in them on account of the high current density at which they are run. The pressure drop in a tinned copper wire immersed in oil at an initial temperature of 108°F. is given in Table VIII. The temperature of the oil is necessarily high under working conditions.

* *Elektrische Beleuchtungsanlagen*, 1903, p. 319.

TABLE VIII.

Showing voltage drop and percentage of fusing current for a Tinned
Copper Wire immersed in oil at 108°F. Normal fusing current of the
wire in air 4 amperes and in oil 18 amperes. Length of wire, 3·3 inches.

Volts across Fuse.	Per cent. of Fusing current.
0·58	18
1.14	29
1·80	39
2·50	49
3.60	65
4·67	78

The oil in such cases gets extremely hot, and in the authors' opinion
no cut-out in which the fuse wire itself is in contact with or immersed
in oil before fusion has taken place should be permitted.
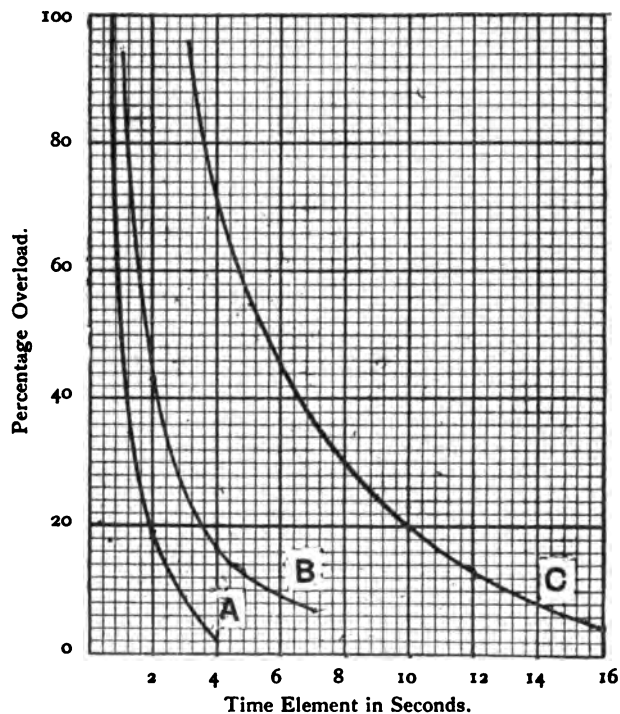
Fig. 20.—Moderate overloads on tinned copper wires, the overload being
taken as excess over the normal fusing current.

A. Normal fusing current of wire 5·45 amps., No. 38 S.W.G.
B.   „   „   „   10·6   „   33   „
C.   „   „   „   54·0   „   21   „

OVERLOAD CAPACITY.

The function of a fuse is to protect the whole of the circuit, including the conductors and the appliances connected to them. Many of these appliances require special consideration owing to their varying capacity for overload. Generally speaking, the capacity of the circuit
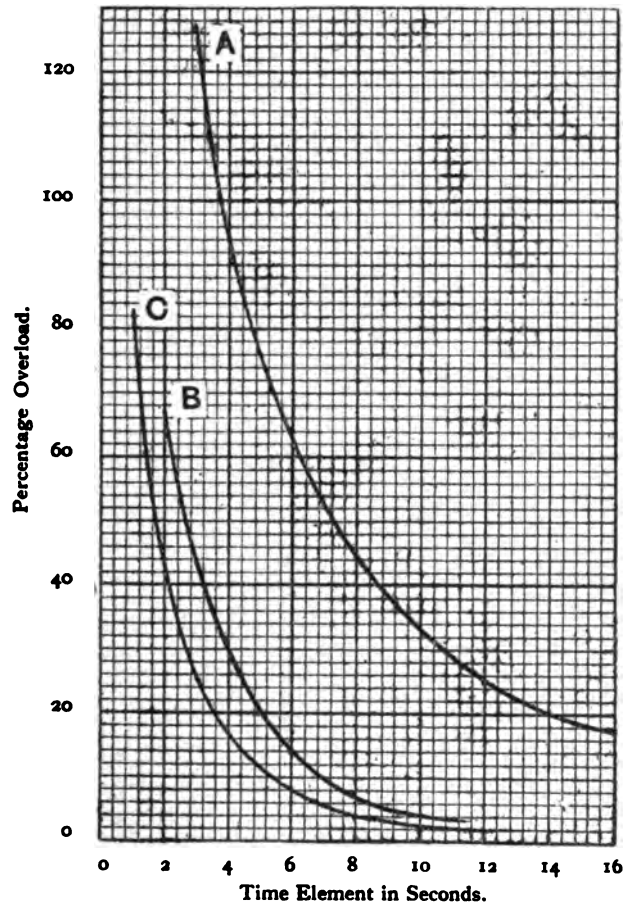
Fig. 21.—Curves showing the behaviour of wires of various materials on moderate overloads, the overload being taken as excess over the normal fusing current.

      A. Tin.
      B. Aluminium, with spring attachment.
      C. Copper and Silver.

Normal Fusing Current for each wire about 10 amperes.

for overload is considerably in excess of the overload capacity of the
fuse which protects it; there are cases, however, which require
special treatment. Arc lamps, for instance, are difficult to deal with,
as they require a fuse which will stand the large current consequent
on starting and the similar current rushes due to the sticking of the
mechanism and other causes. On the other hand, if the fuses are set
to blow with a hundred per cent. excess over the normal working
current, the lamps may easily be burned out with a far less overload
than this if it be continued for some time. It is difficult to see how
the fuse can be set for a lower limit than that stated above without
giving trouble, due to frequent blowing. The remedy seems to lie
in careful and frequent inspection of the lamps. With regard to
motors, the matter is somewhat simpler; the fuse should be set for
100 per cent. excess over the normal working full-load current; it
will then be able to stand the variations in current likely to occur and
to protect the leads from over-heating. For the protection of the
motor from severe overload, the overload release on the starter must
be relied upon. It would be an advantage if these releases could be
adjusted, and then closed or secured so as to be safe from the
attentions of unauthorised persons. Fig. 20 shows the relation
between the percentage overload and the time taken to fuse the
wire from a cold state for tinned copper wires with normal fusing
currents varying from 5 to 54 amperes and a length of 4½ inches.
These curves are for moderate overloads—the maximum being 100
per cent.—the overload in each case being taken as the current in
excess of the normal fusing current and expressed as a percentage
of the latter. Fig. 21 gives a comparison between the overload
capacity of wires of silver, copper, aluminium, and tin, the normal
fusing current of each wire being of about the same value—namely,
10 amperes. The curves show the relation between the time in
seconds and the percentage overload. It will be noticed that tin is
the most sluggish, and copper and silver are the quickest in
action—the two latter being practically equal. Fig. 22 shows the
effect of excessive overloads—up to 2,000 per cent.—on tin wires.
The times were taken on a chronograph drum driven at constant
speed by a motor. The higher values for the currents were obtained
by substituting for the fuse a wire of equal resistance but of greater
carrying capacity and adjusting the current to the desired value by
means of a resistance, and then reinstating the fuse. It cannot
therefore be stated definitely that the current ever reached this
maximum value. It will be seen that the time for fusion decreases as
the overload is increased. This result is borne out by Oelschläger's
experiments with the oscillograph subsequently referred to, although
it is at variance with the conclusions of Stine,* who stated that the

* Stine, Gaytes, and Freeman, *Trans. Amer. Inst. Elect. Eng.*, vol. 12, page 654, 1895.

time of fusion tended to become constant with overloads above a certain value. As, however, his experiments were not carried out with overloads greater than 300 per cent., his deductions are hardly conclusive.

EFFECT OF WIRES IN PARALLEL.

Experiments were made with a tinned copper wire No. 22 S.W.G. diameter 0·074 cms. with a normal fusing current of 49·8 amperes.

Fig. 22.—Excessive overloads on Tin Wires, the overload being taken as excess over the normal fusing current.
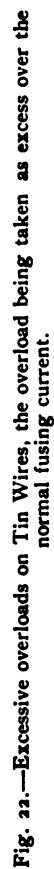
A. Normal fusing current of wire, 44 amps., No. 16 S.W.G.
B.   ,,   ,,   ,,   21   ,,   12   ,,

The wires were arranged in parallel, horizontally $\frac{1}{4}$ in. apart. The results are given in the following table :—

TABLE IX.

Tinned Copper Wires in Parallel.

No. of Wires.	Fusing Current Amperes.	Fusing Current per Wire Amperes.
1	49·8	49·8
2	90	45·
3	130	43·3
4	170·5	42·6
5	218	43·6
6	259	43·1

It will be seen that with three wires and upwards the current per wire is practically constant.

TABLE X.

Effect of Mechanical Injury on a Tinned Copper Wire, No. 33 S.W.G. of Length 3·4in., and a Normal Fusing Current of 10·6 amperes. Wire horizontal.

Nature of Injury	Fusing Current in Amperes.	Remarks.
Wire uninjured	10·6 ...	Normal fusing current
2·7 twists per inch	10·6	
5·5 „ „	10·6	
.10 „ „	10·4	
33 „ „	10 ...	Volts across fuse 1·6
5 twists per inch put on and reversed. Repeated four times. Twist left on	10·2 ...	Volts across fuse, 1·5
12·5 twists per inch reversed and left off	10·5	
1·25 twists per inch put on and reversed 16 times, left off	10·2	
One kink at centre.	10·5 ...	Fused at kink.
Kink half-way between middle and one end of wire	10·6 ...	Fused at centre and not at kink.
Blow near centre	10·6 ...	Did not fuse where flattened by blow.
Two blows, one at each side of centre	10·5 ...	Fused between indentations.
Five blows	10 ...	Fused between indentations.
Wire cut half through	10·4 ...	Did not fuse at cut.
Cut round wire	10·5	
1 loop	10·2 ...	Fused almost invariably where the wires crossed at the bottom of the loop.

EFFECT OF MECHANICAL INJURY.

Experiments were made to determine the effect of twists, cuts, kinks, and blows on fuse wires of copper and lead; the results are embodied in Tables X. and XI.

TABLE XI.

Effect of Mechanical Injury on a Lead Wire. Length, 5 inches. Normal fusing current 35 amperes. Wire horizontal.

Nature of Injury	Fusing Current in Amperes.	Remarks.
Wire uninjured	35	Normal fusing current.
3 twists in 5 inches left on...	35	No effect.
10 „ „ „ ...	35	No effect.
1 twist in 5 inches taken off reversed and again taken off, repeated 6 times, and left off	34·5	Note in all cases the twists were distinctly visible.
1 blow at centre flattened to half thickness	35	Fused at indentation.
2 blows, 1 at each side of centre	35	Fused between indentations.
6 blows	35	No effect.
2 cuts at each end half through wire	35	No effect.
Knife cut at centre	35	No effect.
1 kink	34	

It will be seen from the above tables that the effect of mechanical injury is remarkably small, particularly in the case of lead wire. The same also applies to tin, the results for which are not given here.

DETERIORATION OF FUSE WIRES.

Fig. 23 shows the relative life of a tinned copper wire, No. 33 S.W.G., when run at various percentages of its normal fusing current. It will be seen that per centages greater than 80, the deterioration is very rapid; it is interesting in this connection to note that copper wires attain a red heat with about 75 per cent. of their normal fusing current, and although oxidation commences at rather a lower temperature than this, it does not proceed rapidly unless red heat is attained. This severe oxidation at high overload will cause the fuse to act in a fairly short time if more than 60 per cent. in excess of the rated carrying capacity is used continuously.

EFFECT OF ALTERNATING CURRENTS.

A careful series of experiments on the effect of alternating currents on fuse wires of various materials has been carried out by Jackson and Ochsner* in the engineering laboratory of the University of Wisconsin. In their experiments, wires of iron, german silver, copper, and fusible alloys were placed in series for 550 hours on an alternating current circuit of 110 volts and 125 frequency with 60

per cent. of their rated current passing continuously. Careful determinations of their resistances were made at regular intervals, but disclosed no appreciable rise within the time named. Of six samples tested for variation in fusing current after the 550 hours run against unused lengths of the same wires, four samples showed an
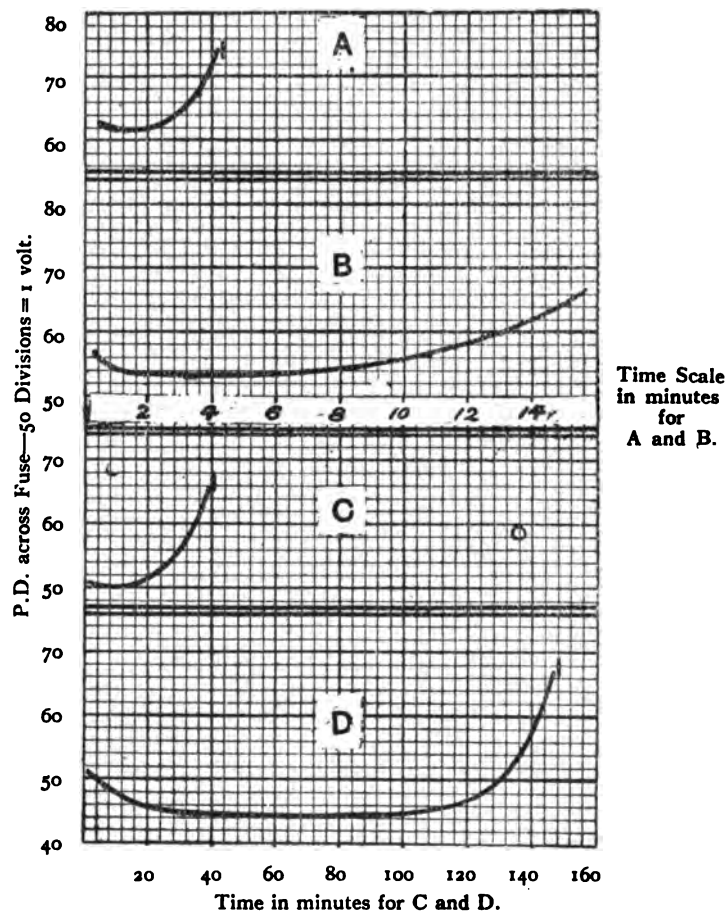
Fig. 23.—Curves showing deterioration of a Tinned Copper Wire, No. 33 S.W.G. Wires horizontal. Normal fusing current 10·6 amperes.

Curve A. Current = 94·5 per cent of normal fusing current.
  „   B.   „   = 89·5 „   „   „   „
  „   C.   „   = 84   „   „   „   „
  „   D.   „   = 80   „   „   „   „

average lowering of 1·18 per cent., and two a slight rise of 1·22 per cent.

SHORT CIRCUITS.

Although a fuse may operate quite successfully with 100 per cent. excess current, it has in practice to face the severe conditions of a short circuit. That these conditions are severe is well known, but the magnitude and time duration of the current rush and the voltage rise on the rupture of the circuit are not so well known to most engineers. The term "short circuit" is a relative one; for instance, a wire which fuses normally with 40 amperes might be said by some to be short-circuited when a current of 250 amperes passed through it, whereas on a dead short the current through it would, under certain conditions, be between 800 and 1,000 amperes. The behaviour of a fuse when short-circuited through a resistance which limits the current to an excess of 20 per cent. of the normal fusing current is very different from the effect observed with currents five or six times as large, and this again differs very considerably from the effect of a dead short circuit. A tinned copper fuse melting with a current about 20 per cent. in excess of its normal fusing current exhibits a greater tendency to arc than when melting under a current of four or five times this strength. This is due to the fact that with a small overload the wire will fuse first over a short length at its centre, and an arc will be formed across this small gap. This gap will increase as the ends of the wires are burned back, until the arc finally fails. With a large overload the heating of the entire wire is so rapid that fusion takes place along its whole length, and the wire is completely disrupted from terminal to terminal. Mr. H. A. Ratcliffe, of the Testing Department of the Manchester Corporation Electricity Works, who has had a large experience of fuse testing, has found that numbers of fuse fittings, which have successfully withstood a so-called short-circuit test with a current limited to seven or eight times the normal fusing current, were entirely destroyed on a direct short circuit. The fuse wire employed in these cases was tin, which, on fusing, is far more favourable to the formation of an arc than is copper. He has also found that on short-circuiting a 50-ampere fuse with an 800-ampere circuit-breaker in the circuit, that the breaker has been opened. That very large currents do pass under short-circuit conditions may easily be shown by short-circuiting a large fuse through a small one in series with it. In this way the authors have fused five copper wires in parallel, fed through a single wire of the same diameter, length, and material, the single wire, of course, fusing as well as the others. The powerfully destructive effects of the true short circuit are due in the first place to the large current which passes, which is limited only by the self-induction and

resistance of the circuit. Where the fuse is directly connected to supply mains fed by a number of generators of large capacity in parallel, the resistance of the circuit will be extremely small, and the current rush proportionately large. Secondly, the inductive voltage rise, due to the breaking of this large current in a small fraction of a second, is very considerable, and materially affects the formation of an arc. Oelschläger* has recently measured, by means of the
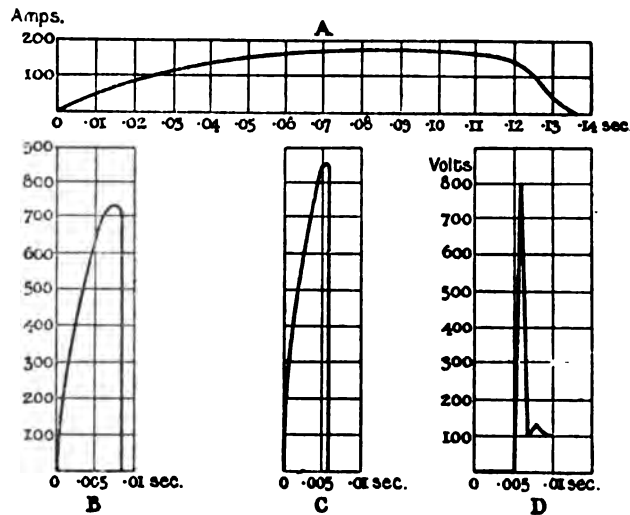
Fig. 24.

oscillograph, the current, pressure rise, and time of fusion on short circuit in a Siemens-Schuckert cartridge fuse with a normal fusing current of 40 amperes. His results are as follows :—Fig. 24, curve A shows the effect of limiting the fusing current to 180 amperes by means of a resistance. The circuit voltage was 110 continuous current, the limiting resistance o·6 ohm, and the inductance 2·5 henry. Capacity of generators 1,000 k.w. at 110 volts. An examination of this curve shows that from the time of closing the switch the current increased gradually, reaching the maximum value to which it was limited by the resistance in o·08 sec.; it then remained constant for o·04 sec.; while the time in which the actual rupture took place was o·02 sec. Further experiments were made with diminished resistance, and self-induction curve B shows the effect with a resistance of o·01 ohm in series, and no artificial self-induction in the circuit. Curve C shows the magnitude of the current rush on direct short circuit, the artificial resistance being removed. As the

resistance of the external circuit becomes smaller, the resistance of the fuse itself becomes relatively more important. The resistance of the fuse, which in this case was of silver, with a melting point in the neighbourhood of 1,000°C., was, when cold, 0·0054 ohm. The resistance of the fuse wire when hot was obtained by raising the current gradually to a point just short of the normal fusing current of the wire, and was found to be 0·017 ohm. On a short circuit, with 110 volts neglecting the resistance of the leads, the maximum current would be $\dfrac{110}{0·017} = 6,500$ amperes. As a matter of fact, the current was found to be only 850 amperes. This is due to the natural self-induction of the circuit and the consequent relatively slow growth of the current, and also to the fact that fusion took place long before the current could reach its theoretical maximum value. The pressure rise, due to short circuit, is shown in Fig. 24, curve D. It will be noticed that at first the pressure across the fuse is practically nil, corresponding to the pressure loss due to a current of several hundred amperes in a resistance of 0·0054 ohm. Just before the melting of the wire the pressure rises to about 25 volts. At tne moment of melting an enormous rise of pressure suddenly takes place, the total voltage being about 800, or nearly 700 volts above the pressure of the circuit. The actual breaking of the circuit took place in 0·00015 sec., the self-induction of the circuit being of the order of 10^{-4} henry. After a small surge the pressure fell to 110 volts, the normal voltage of the circuit. In order to see whether the self-induction of the source of current (machines) had any effect upon the results, the experiments were repeated with a 110-volt battery giving 400 amperes. Curves of the same character were, however, obtaind.

CONNECTION BETWEEN NORMAL FUSING CURRENT AND LENGTH OF BREAK.

It is frequently stated that there is no rational connection between the length of break or distance between the terminals of a fuse and the normal fusing current of the wire. It is a common practice, however, to increase the length of break with the normal carrying capacity of the wire, and this usage may be defended on the following grounds : On a short circuit, as has already been pointed out, the current is prevented from reaching the immense value to which it could theoretically attain by the fusion of the wire; it is evident, therefore, that the larger the wire employed, the greater the current will be before fusion takes place, and the inductive pressure rise, when the rupture of the circuit does take place, will be dependent upon the current passing at the time, and the time in which this current is broken. This inductive pressure rise will largely influence the formation of the arc, and the length of break must

therefore be increased when large currents are to be broken on the fuse. As the voltage of self-induction is dependent on the rate of decay of the current, it is possible that with large wires and open-type fuses this will be slower owing to the large mass of metal volatilised acting as a conducting bridge, and that in consequence the voltage rise will be less. In the opinion of the authors the normal fusing current in copper fuses should not exceed 100 amperes per wire. Fuses for larger currents should be made up of several wires in parallel, spaced about half an inch apart. Under these circumstances, although the mass of metal employed may be large, it does not seem probable that the time of decay of the current would be increased, provided, of course, that a proper length of break has been allowed. The double rôle which a fuse has to play in breaking the circuit with a pre-determined current and suppressing the consequent arc undoubtedly militates against its reliability in the performance of the first function. The effectual suppression of the arc in some circumstances calls for the proximity of masses of cold material, such as porcelain, or the passage of the wire through asbestos or other incombustible material. If the wire is in contact with any such bodies for a part or the whole of its length, its fusing current will be affected to a greater or less extent. The authors find, however, for pressures up to 220 volts tinned copper wires in porcelain clip holders in which the wire is free in air for a length of 2½ inches between the terminals are quite satisfactory on a dead short circuit. For distribution boards the spacing should be rather more liberal than is at present customary, and the fuses should be screened from one another by septa of incombustible material to limit the spread of the molten metal. Wherever possible the contacts and terminals should be screened from the action of the arc.

FUSE METALS—TIN AND LEAD.

In the early forms of fuse, lead and lead alloy wires were used as they melted at low temperatures, and were therefore considered to be less likely to set fire to inflammable material in their immediate neighbourhood than wires of a metal with a higher melting point. It is, however, quite an easy matter, under suitable conditions, to raise wires of these metals to a temperature very much higher than that of their melting point—namely, to a bright red heat. A further disadvantage is that owing to their comparatively poor conductivity a larger mass of metal has to be employed to carry the normal working current than is required in the case of wires with a high conductivity, so that the mass of metal disrupted when fusion takes place is consequently much larger and the probability of the formation of an arc much increased. The arc is much more persistent with these metals than with copper, so much so that fuse fittings

that will stand a direct short circuit with copper wire may be destroyed when used with tin or alloy wires. This is probably due, as already pointed out, to the larger mass of these metals present and to a greater proportion of it being vaporised than in the case of copper. When a copper fuse is disrupted the greater part of the metal is scattered in the form of globules, and only a small quantity seems to be vaporised. The blowing of a copper fuse may be said to be "clean" compared with that of the metals under consideration, which is accompanied by a quantity of heavy fumes which are deposited on contiguous cold surfaces. These deposits are often difficult to remove, and certainly facilitate the formation of an arc for fuses that are subsequently blown in the same holder. Although the metal pellets from the fusion of these metals are not so hot as the globules from a copper wire of the same carrying capacity, and they are, moreover, not scattered so far, yet the display of "fireworks on a dead short circuit is considerably greater. Further, these metals are soft, and although, as has been shown, the effects of mechanical injury are not as great as might have been expected, severe cutting may take place at terminals unless the wires are soldered to copper or other suitable lugs. The cooling effect of the terminals is also considerably greater in the case of lead and tin than of copper. In the case of alloys it is also difficult to secure the constancy of their composition as supplied commercially, and the alloys themselves are liable to change their structure, either due to the passage of the current through them or to the effect of repeated heating and cooling. These metals also become very brittle at a temperature slightly below their fusing point. The authors' experiments show that if they are subjected to vibration when in this state the fusing current is lowered by about three per cent. They are also liable to severe oxidation, with a consequent large increase of the current-carrying capacity of the wire under overload.

SILVER

can be easily obtained of standard composition, is comparatively hard, of high conductivity, is not easily oxidised, and on fusion does not give rise to heavy vapours, and therefore does not encourage the formation of an arc. Against these advantages may be set its cost, and the fact that unless enclosed it is liable to have its surface converted into sulphide. Silver fuse wire is used very largely in plug and cartridge fuses for installation work in Germany, where Britannia metal is also employed. Silver wires act more promptly than wires of lead or tin (see Fig. 21). If a silver wire be placed in series with a lead wire of the same carrying capacity, in most cases the silver wire will be found to have opened the circuit cleanly and

decisively, while the lead fuse has remained unmelted.*

ALUMINIUM, ZINC AND CADMIUM.

These metals possess valuable non-arcing properties, but require special arrangements, which are more or less troublesome; the two latter are also mechanically weak, and cannot be obtained in the form of wire.

COPPER.

The authors strongly favour the use of tinned copper. It is easily obtainable of constant composition. It is mechanically strong, and the mass of metal required for a given carrying capacity is small. Care must be taken with the smaller sizes to see that the wire itself does not get into the thread of the terminal screws, otherwise it is easy to handle in sizes down to No. 38 S.W.G., which would be used to protect a three-ampere circuit. It does not oxidise perceptibly when carrying 50 per cent. of its normal fusing current, but at higher rates than this oxidation becomes troublesome. There is, however, no trouble from the holding up of the molten metal by the film of oxide. Unless guarded the molten particles may, on a dead short circuit, be scattered 15 or 20 feet, but this difficulty may be easily overcome by suitable protection. Considerable prejudice seems to exist against copper fuses on account of alleged increased fire risk. The risk of fire is threefold—first, owing to the wire becoming red hot prior to fusion; secondly, due to the scattering of the molten particles of metal; and, thirdly, owing to the formation of a persistent arc on fusion. With properly designed holders and fuse-boxes, in which all inflammable material is entirely excluded from the sphere of action of the wire, the fire risk from the first two causes is practically nil; while, as has been already pointed out, the risk from the third cause is less with copper than with more volatile metals.

CONSTRUCTION OF FUSES.

The early forms of cut-out in which soft metals were employed were particularly prone to trouble at the contacts due to oxidation or the loosening of the contact owing to the different coefficients of expansion of the metals forming the terminals and the fuse wire. Soft wires are now generally soldered to copper or brass contact pieces. It is very desirable that fuses should be easily removable for inspection and renewal, and be capable of being quickly replaced on a live circuit without shock or injury to the operator. This necessitates the fuse wire being mounted in a removable holder of insulating and incombustible material. Some of the various forms of contact in use between the fuse-holder and the circuit terminals are shown in Fig. 25. Fuse-holders may be divided into three classes, according to the environment of the wire, as follows :—(1) Open type; (2)

* *Elektrotechnische Zeitschrift*, vol. 19. p. 591, 1898.
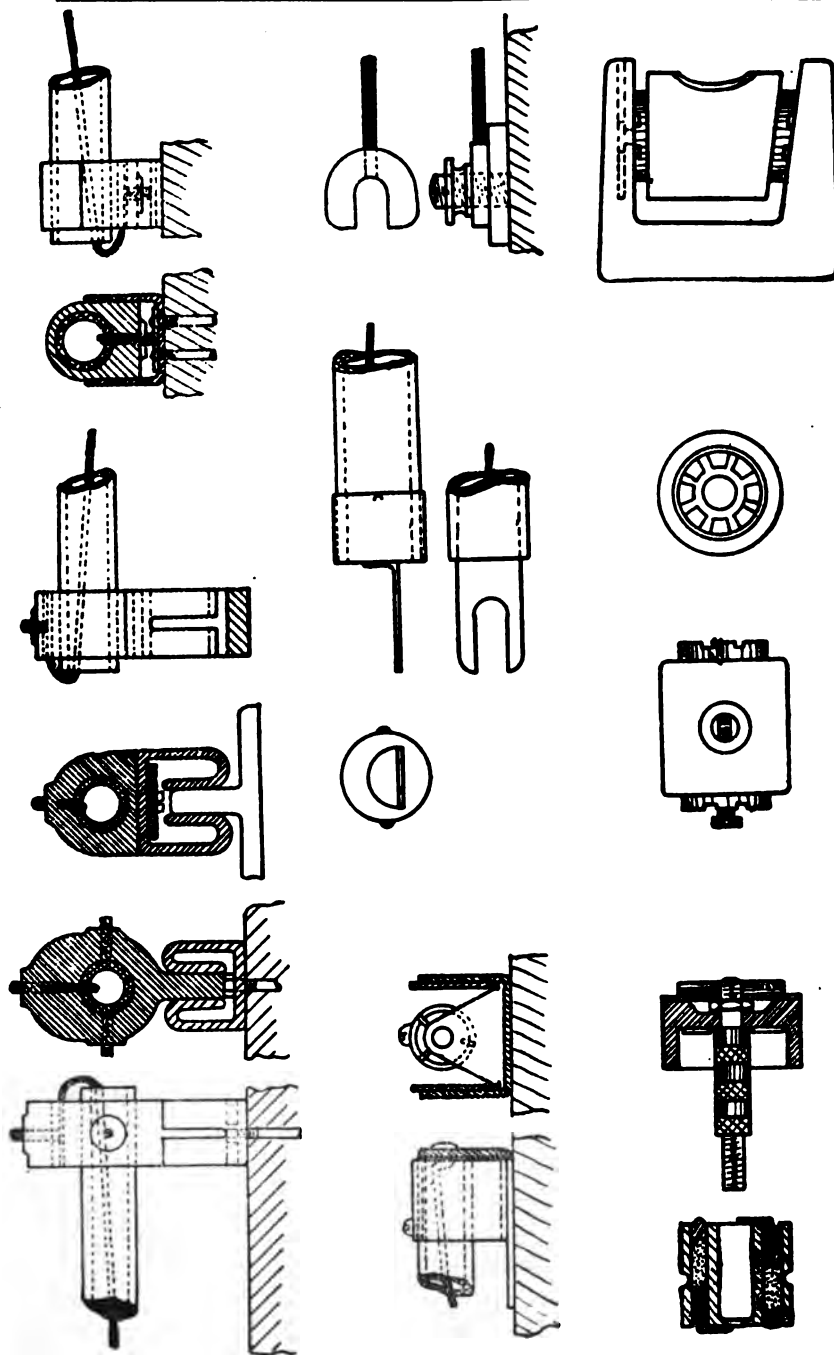
Fig. 25.

semi-enclosed; (3) enclosed. In the open type the wire is free in air from terminal to terminal; in the semi-enclosed type the wire may be free in air for its whole length, but is surrounded by an incombustible and insulating tube of small or large diameter, or it may be passed for a small portion of its length—usually at its centre—through a hole or channel of small diameter in the porcelain holder or through a wad or washer of asbestos or other incombustible material. In the enclosed type the wire is enclosed in a tube or envelope of fibre or porcelain and packed closely round with refractory insulating material. Whatever the environment of the fuse may be, it is desirable that it should be kept as constant as possible if the fusing current is to be in accordance with a pre-determined value. Where the wire is free in air its fusing current may be determined from the authors' formulæ, provided the limiting conditions are observed. Whenever the wire comes into contact with porcelain or other material its contact should be of a definite and constant character. The fusing current of the wire in the holder may then be determined by direct experiment. It must be borne in mind that fuse wires increase considerably in length before fusion takes place, and that in consequence they may sag or bend, and so come into contact with the holder. Where the enclosing tube is of vulcanised fibre a contact with the wire will lead to charring and possible firing on overloads.

SEMI-ENCLOSED FUSES

should have the holders so constructed that any deposit of metal vapour or oxide upon them, due to the blowing of the fuse, can be easily removed. Rigid asbestos tubes should either be discarded when fouled, or be provided with removable asbestos paper liners. Short lengths of loosely woven asbestos tubing, which can be slipped over the wires, and which fit them freely, give excellent results for the larger sized tinned copper wires, damping out the arc and limiting the scattering of the molten metal; allowance, however, must be made for the effect on the fusing current. Although the semi-enclosed fuse prevents the indiscriminate scattering of the molten particles on short circuit, yet nothing short of complete enclosure will prevent the metal being blown out of the open ends of the tube or holder. Fuses of this type at present on the market may be said to successfully withstand short circuit at higher voltages than the open type, although in most cases their fusing current is somewhat unreliable.

ENCLOSED FUSES.

Enclosed or cartridge fuses, in which the wire is surrounded by a tubular sheath with closed ends, have been developed from the Edison plug fuse. The tubes are usually loosely packed with an

incombustible filling. Although the primary function of the filling is to smother the arc, it has also an important effect in reducing the
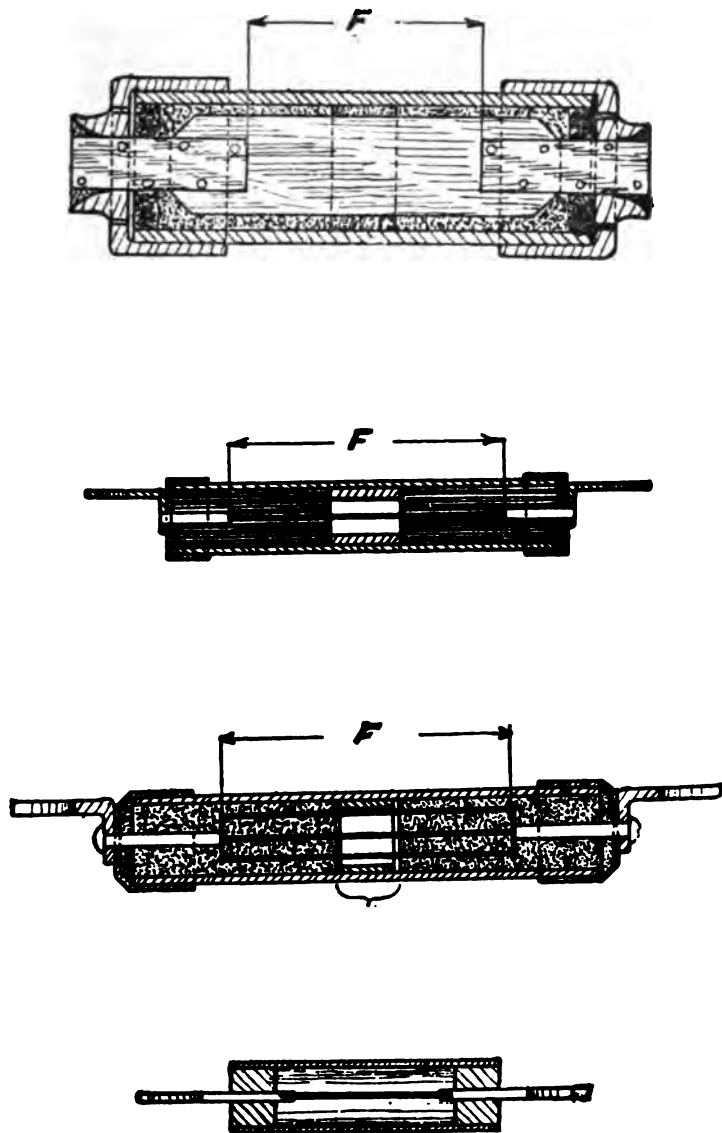
Fig. 26.—Enclosed Fuses.

violence of the explosion on short circuit. This is due to the heated gases being driven into the interstices of the filling and being thereby rapidly cooled. At the present time these fuses may be divided into two classes according as the fuse is entirely surrounded by the filling along its whole length, or is passed through a small air chamber usually located at its centre, the remaining spaces being occupied by filling. The construction of some American types is shown in Fig. 26. In the packed fuse it is evident that the molten wire receives a considerable amount of support from the filling material, and in consequence it may retain its continuity until it is volatilised, when it

Fig. 27.—Siemens Cartridge Fuses (large size).
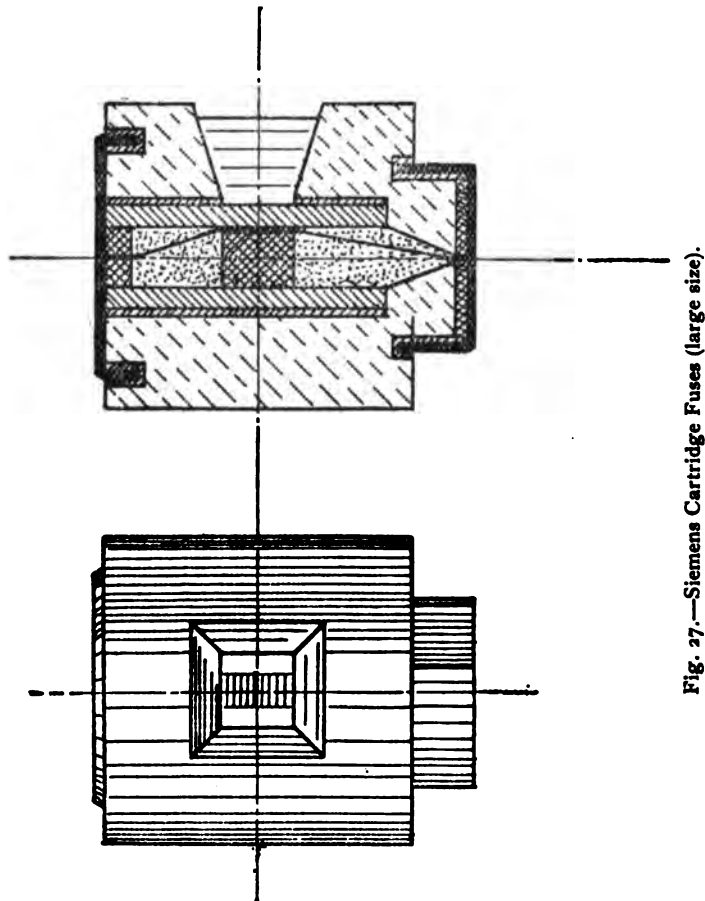
may be carrying a current large enough to give rise to unpleasant effects, both in the circuit and in the fuse-holder itself. With a short length of the wire passing through a central air-chamber the wire has a better chance of rupturing, provided that the length of wire in the chamber is not too short, and that the metal employed is not too easily oxidised. Sachs* makes a great point of surrounding the wire with a material capable of entering into active combination with it when in the molten state. He mentions borax as an ingredient which acts as a flux on the oxide coating, and states that the other ingredients require careful selection. An analysis of the filling in two types of enclosed fuse obtainable in this country disclosed in one case nothing more startling than mixture of crushed limestone with (probably) fireclay or ground slag. It is difficult to see what chemical action·such a mixture could have upon a zinc strip, which was the material used in this instance. In the second case where tin-lead alloy wires were employed, the filling consisted of about 50 per cent. sodium carbonate and 50 per cent. bone ash. As bone ash, however, only absorbs lead oxide freely at a temperature between 900° and 1000°C., the wire would have to be raised to this extremely high temperature before absorption would take place. It seems probable, therefore, that the action of the filling is largely mechanical, and also that owing to the decomposition of an ingredient such as sodium carbonate gas may be given off, and so render the thread of molten

Index wire under paper
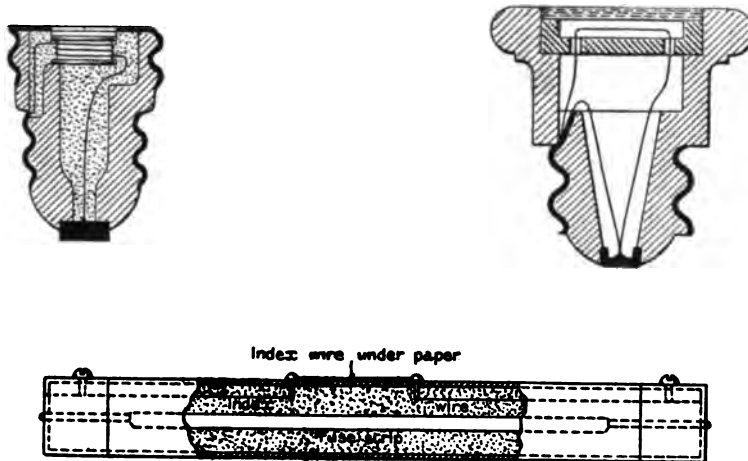
Fig. 28.

metal discontinuous. The Germans have developed very complete systems of cartridge fuses in which emery and French chalk are used

* *Journal Amer. Inst. Elec. Eng.*, vol. 16, page 131, Feb., 1900.

as fillings, and porcelain as the jacket material. These fuses are extremely compact, and are non-interchangeable, both for voltage and current-carrying capacity. The construction of the large size Siemens cartridges is shown in Fig. 27. With enclosed fuses of all kinds it is necessary to have an indicator to show whether the fuse has blown or not; this usually takes the form of a very fine wire in parallel with the fuse wire, and arranged so as to be visible to the operator. Examples of these indicating devices are shown in Fig. 28. The subject of enclosed fuses is a somewhat wide one, and the authors hope to make it the subject of a separate investigation, and prefer for the present not to express any more definite opinions in the matter.
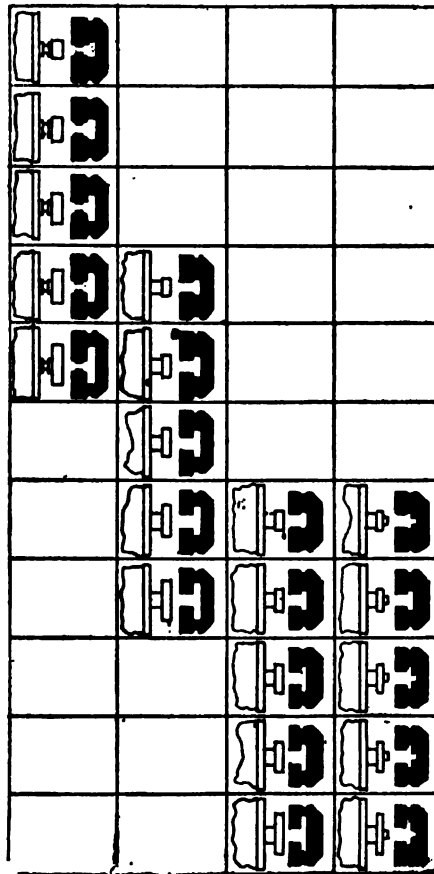
Fig. 29.

GENERAL CONSIDERATIONS.

Tinned electrolytic copper should be used exclusively, except in the case of enclosed fuses which have been designed for use with metals of a low melting point. All fuse-holders should be marked with their normal carrying capacity in amperes (50 per cent. of the normal fusing current*), the voltage of the circuit for which they are intended and the gauge of the wire employed. Fuses should be screened from each other by incombustible septa either on the holder or between the fuses. Distribution boxes should have ample air space, and be lined with incombustible material, such as asbestos or Uralite on exposed wood surfaces. The length of clear break or the minimum distance from metal to metal of the terminals should not be less than 2½ inches for circuits up to 220 volts for open fuses up to 20 amperes, with an additional half inch for every 15 amperes up to 110 amperes. Small fuses should be non-interchangeable, both for voltage and fusing current. There does not seem to be any necessity to extend the non-interchangeability for current to the larger sizes where special fittings are necessarily employed, and probably the following ranges should suffice :—

Normal fusing } current } 3, 5, 10, 15, 20, 30, 45, 60, 80, 100 amperes.

Non-interchangeability may be secured in a number of ways. In the method adopted by Mix and Genest for their plug fuses, the plugs are fitted with a specially profiled ring which has to pass through a template of the same shape in the socket before the plug can be screwed home. Fig. 29 shows a range of slots through which the contact pins of the large size Siemens cartridges have to pass. These cartridges are for use with the inclined jaws shown in Fig. 25. The non-interchangeability of these fuses from o·5 to 10 amperes has been effected in a very simple manner, Fig. 30, by making the lower contacts in the form of a round pin, the diameter of which is different for different currents, and by providing the bases with gauge rings which fit the pins. For higher voltage the cartridges have stepped pins and rings with raised rims, as shown in the figure. Contrasting the open and semi-enclosed types with the cartridge type for distribution boards for lighting purposes, the latter type is certainly more costly for replacements, and also for first cost, although as things stand at present it presents several advantages over the systems in vogue. A double-pole distribution board of this type with four branches is shown in Fig. 31. For outside work the cartridges can be placed in bell-shaped insulators, which act as weather covers, Fig. 32. In this country we are accustomed to regard the fuse-holder

* For large fuses of several hundred amperes it is not necessary that the fuse should be set for as much as 100 per cent. excess current, as such circuits usually include an ammeter and are under some sort of supervision.

Fig. 31.
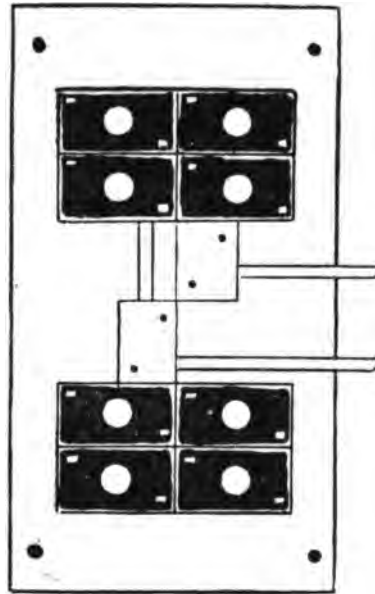
Fig. 32.
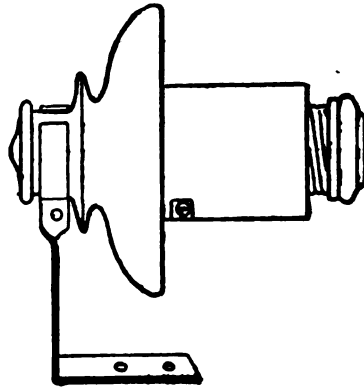
Fig. 30.
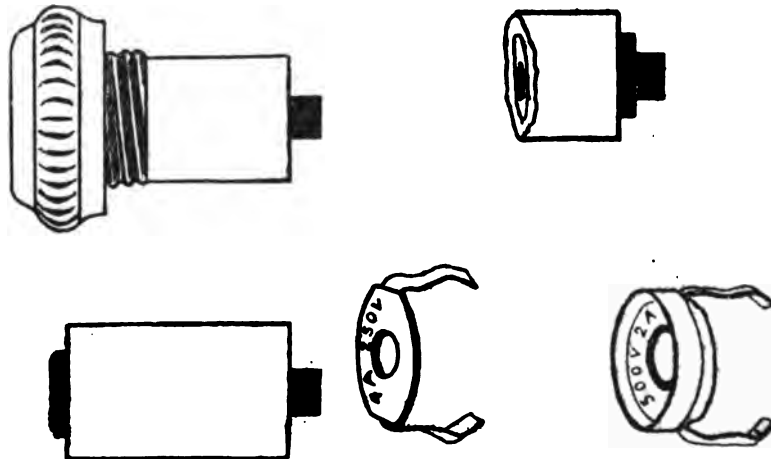
as a permanent fitting, and like to replace the wire ourselves when the fuse blows—not infrequently with a larger size of wire. Our system has its advantages, and if made to conform with a set of regulations issued by this Institution for the construction and testing of fuses should prove quite satisfactory. With regard to house service boxes, the box should be of metal with a lining of insulating and refractory material capable of resisting the action of an arc. Many of the enamels now used are liable to chip off when heated locally, with the result that the arc often gets through to the case. Ample air space should be allowed between the fuse fittings and the inside surfaces of the box. The question of air space is important with reference to the persistence of the arc. The heated air and vapour should be given a chance of getting away. In this connection there is no reason why screened vent-holes should not be employed; this would promote a rush of air which should tend to rupture the arc. With open fuses in metal boxes the break should be at least 4½ inches. For house and motor services the enclosed fuse seems to offer considerable advantages over other types where large currents are required, and with pressures up to 400 volts, their chief drawback at present being the difficulty and cost of refilling the cartridges.

TESTING OF FUSES.—NORMAL FUSING CURRENT TESTS.

In order to secure a common basis for the testing of copper fuse wires for normal fusing current, experiments were made to determine the ratio between the current necessary to bring a given wire to a red heat (in diffused daylight) and its normal fusing current. As expected this ratio was found to be constant, being equal to 0·75 for tinned copper wires of such length as to be independent of the cooling of the terminals. The normal fusing current of a wire of given length and environment has already been defined as "the minimum current required to fuse the wire in such a time interval as shall be necessary for the wire to have attained its maximum steady temperature." If, therefore, we raise the wire rapidly up to red heat we know that it is then carrying about 75 per cent. of its normal fusing current; the remaining 25 per cent. must then be added gradually at such a rate that the wire can attain a steady temperature as the current is increased. Large wires naturally require a longer time for this purpose than small ones. Open-type fuses in which tinned copper wire is employed should be tested for normal fusing current in the following way :—The wire in its holder should be screened from draughts, and the current raised until the first appearance of redness at the centre of the wire is observed in diffused daylight; this is the "red-heat current," and should be noted. The wire should be brought up to redness fairly rapidly—say in half a minute. For wires

with normal fusing currents up to 20 amperes (up to No. 24 S.W.G.) the current should then be gradually and regularly increased at the rate of $\frac{1}{30}$th of the "red-heat current" per ten seconds. For wires with normal fusing currents from 20 to 120 amperes (Nos. 24 to 26 S.W.G.) the current should be increased at the rate of $\frac{1}{40}$th of the "red-heat current" per ten seconds. The above method of procedure will be found to allow ample time for the wires to attain a steady temperature. For semi-enclosed and enclosed fuses the time interval necessary to bring them up to a given temperature will depend upon the environment of the wire, and should be ascertained by experiment. Sachs* made experiments to determine the carrying capacity of fuse strips such as used in his solid packed "no ark" fuses, when covered with the environment, and when entirely air-surrounded and exposed; he has shown with the several sizes of strips tested that the current-carrying capacity of the strip is the same whether it is encased or not. The smaller fuse strips show a slightly increased capacity when encased. His results are shown in Table XII.

TABLE XII. (SACHS).

Rating Tests of 500 volts 40 amperes Fuse Strips.
Fuse and terminal wires $5\frac{3}{4}$ inches between contacts.
Distance between centres of posts, $6\frac{3}{4}$ inches.
Terminals, 0·11 inch diameter.

	Tube	Fuse.	Filling.	Run at Amps.	Time.	References.
Enclosed	$\frac{3}{4}'' \times 5\frac{3}{4}''$ ...	·018 × ·13 × 3" ...	All active	40 ...	1 hr. ...	
	...	"	...	50 ...	55 sec.	... Opened.
	...	"	...	50 ...	$3\frac{1}{2}$ min.	... Opened.
Exposed to Air.	None. ...	"	... Air	40 ...	15 min. ...	
	...	...	"	50 ...	12 sec.	... Opened.
	...	...		50 ...	25 sec.	... Opened.

It would appear, from a consideration of the above table, that for enclosed fuses with a certain overload, that the ratio of the time interval for blowing when in a hot and cold state respectively is about 1 to 4, whereas with the strip exposed to air it is about 1 to 2.

SHORT-CIRCUIT TESTS.

Short-circuit tests on fuses should be made as far as possible under actual working conditions, and with a voltage 10 per cent. in excess of the circuit voltage for which the fuse is intended. It has been shown that the current rush on short circuit may be as much as twenty times the normal fusing current of the wire or forty times its normal carrying capacity when rated to blow with 100 per cent. excess current, so that in order to simulate working conditions a current of this magnitude should be arranged for. This may be done by substituting for the fuse a length of wire of greater carrying

* Trans. Amer. Inst. Elect. Eng., vol. 17, page 131. Feb., 1900.

capacity, but of approximately the same resistance, and adjusting the current through this to the desired value by means of a regulating resistance and an ammeter, then replacing the fuse and short-circuiting through a heavy switch. In no case should the short-circuit current be arranged for less than 400 amperes. The source of current and the resistance of the conductors must be so arranged that up to the moment of melting of the fuse the total drop of pressure shall not exceed 2 per cent. Wherever possible facilities should be given at the central station or one of the sub-stations serving the district for testing of types of fuses proposed for consumers' premises. In this case the pre-arrangement of the short-circuit current may be dispensed with and the fuse connected with heavy leads to the mains or bus-bars, arrangements being made for switching in or out as desired. Where fuses are proposed to be used on each pole of a circuit they should be tested in series. House service fuses should be tested with the box covers in position. Fuses should also be tested for arcing with currents slightly in excess of their normal fusing current, the current being increased gradually in the way already specified for determining the normal fusing current.

CONCLUSION.

It has been shown that a fuse wire may be subject to a number of influences which affect its fusing current to a greater or less extent. Most of these disturbing effects are small, ranging from about 3 to 12 per cent., and it may be urged that with a device which becomes operative with excess currents of 100 per cent., errors of the order named may be safely neglected. If these sources of error were present singly this might be so, but this is rarely the case, and it is to the accumulated effect of several of them operating together that so-called unreliability of fuses is due. Maximum errors due to various causes in open and semi-enclosed types of fuses are scheduled below.

Maximum per cent. error.

Preece's Formula : Re-determined values.

	Maximum per cent. error.
Tinned copper wires at 100 amperes.........	19 per cent. high.
" " " 20 "	Correct.
" " " 3 "	20 per cent low.

Vertical as against horizontal position.

Tinned copper .... 5 per cent.

Effect of length and cooling due to large terminals. Percentage increase over fusing current for a length which is independent of cooling of terminals.

Lengths.

Tinned Copper.	6″	5″	4″	3″	2″	1″
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
For 115 amps.	2·5 ...	6·5 ...	15 ...	31 ...		
For 10 amps.		...	...	...	2 ...	5 ... 30

Effect of Terminals. Increase in fusing current for heavy terminals as against light ones for tinned copper.

For 115 amps. length 4½ inches .... 6 per cent.

„ 10 „ „ 2½ „ .... 3 „

„ 10 „ „ 1½ „ .... 5 „

Vibration. Tin and lead, decrease in fusing
current .... 3 „

Enclosure in tubes. Decrease in fusing current 12 „

Contact with porcelain.

Tinned copper in semi-enclosed porcelain fuse-holder :—

(1) Wire arranged so as not to touch the porcelain, increase above normal fusing current = 2 per cent.

(2) When pulled tight and close to porcelain FC increased 10 per cent.

Lead wire arranged as above in (1) increase in FC = 18 per cent.

Arranged as in (2) above, increase = 52 per cent.

Tinned copper in holder of damper type :—

Wire out of contact with porcelain, FC increased 5 per cent.

Wire in contact with porcelain, but without damper, FC increased 14 per cent.

Wire in contact with porcelain and damper, FC increased 24 per cent.

The fuse is an extremely simple device, and it is perhaps due to this fact that it has not been treated with the necessary care. All experiments with fuses should be carried out with the greatest care if accurate results are to be obtained, and the same care should be exercised in their design and installation. The authors' thanks are due to the Committee of the Municipal School of Technology, Manchester—in the electrical laboratories of which institution these tests were carried out; and to Messrs. C. C. Metcalfe, F. Morton, J. and R. Cunliffe, and B. E. Stott for assistance in the experimental work; to Mr. Bertram Stott for assistance in the preparation of the drawings; and to Mr. E. L. Rhead for the analysis of the materials.

Their thanks are also due to Mr. S. L. Pearce (the City Electrical Engineer), Mr. S. Skinner, the Siemens Electric Appliances Ltd., Messrs. Drake and Gorham, Veritys, Dorman and Smith, and the General Electric Company for the loan of fittings and fuses.

ANALYSES.

Report by Mr. E. L. Rhead, of the Metallurgical Department of the Municipal School of Technology, on the composition of samples of fuse wires employed by the authors, and on the fillings for enclosed fuses.

Low Tension Thermal Cut-outs

Thick Tin Wire.

Constituents found per cent.

	Per cent.
Lead	0.201
Copper	0·280
Iron	0·035
Zinc	traces
Arsenic	traces
Tin (a)	99·4

Thin Tin Wire.

	Per cent.
Lead	0.131
Copper	0·118
Iron	0·086
Zinc	traces
Arsenic	traces
Tin (a)	99·75

Aluminium Wire.

Iron	0·098
Calcium	0·09
Magnesia	0·034
Silica	traces
Alkalis	traces
Aluminium	99·8

Copper Wire (Tinned).

Tin coating	0·51
Iron	traces
Arsenic	traces
Copper	99·44

Filling for Enclosed Fuses.

Sample A White powder—

	Per cent.
Soluble in water after drying	49·17
Insoluble	50·83

The Soluble part is Sodium Carbonate.
The Insoluble part is Phosphate of Lime (Bone Ash).
The Powder contains no Borax.

Sample B Grey powder—

	Per cent.
Soluble in Water	0·050
Insoluble in Water	99·95
Soluble in Hydrochloric Acid	63·81
Insoluble in Hydrochloric Acid	36·19
Soluble Silica	0·885
Ferric Oxide and Alumina	14·98
Lime	24·35
Magnesia	1·835
Carbon dioxide	21·2
Phosphoric Acid	traces

Free metallic iron exists in the material.

ZINC AND ALUMINIUM FUSES.

The authors have thought it desirable to extend the examination of zinc and aluminium as materials for fusible cut-outs. Both these metals are in use to a considerable extent at the present time in fuses of large capacity. Zinc cannot be drawn into wire and can only be rolled hot, while aluminium wire, as previously shown, particularly when of small diameter, is unreliable as a fuse owing to the molten metal being held up by the skin of oxide. For example, an aluminium wire ·7 mm. diameter, when supported between terminals in the ordinary way, will disrupt with 43 amperes, whereas the wire really melts within its oxide skin with 21 amperes, and the wire could be ruptured at this current value by means of the repelling action of a magnet or the tension due to a weak spring. It is evident, then, that only in the form of strip can zinc and aluminium be advantageously employed as fuses. The examination of copper and lead strip for the purpose of connecting the fusing current with the dimensions of the strip employed showed that this relation was expressed by rather different formulæ in the two cases. With copper strip the fusing current is proportional to the breadth with a constant thickness, and the curves connecting these quantities when plotted all pass through the origin; if, however, we plot thickness against fusing current for strips of constant breadth, it will be found that the curves pass through a point on the axis of thickness considerably to the left of the origin, due to the increased carrying capacity per unit area in the small strips, owing to their relatively greater cooling surface. In the case of lead strip, the curves connecting fusing current and breadth when extended backwards are, for a similar reason, found to cut the axis of breadth at a point considerably to the left of the origin, while on plotting fusing current against thickness for a constant breadth the curve is found to follow a logarithmic law, that is to say, with a constant breadth the fusing current is not proportional to the thickness "t," but to "t^n" (for lead $n = ·74$).
This may be summarised thus :—

Breadth.	Thickness.
Copper, $c \propto b$	Copper, $c \propto (t + k_2)$
Lead, $c \propto (b + k)$	Lead, $c \propto t^{·74}$

Where c = fusing current,
b = breadth,
t = thickness.

Now, the melting point of zinc and its current density at fusion is intermediate between those of copper and lead, and the law connecting its fusing current and dimensions may be regarded as being intermediate between those given above; in fact, for zinc strip—

$$c \propto (b + b_1)$$
$$c \propto (t + t_1)$$
$$\text{or } c = \kappa (b + b_1) (t + t_1)$$

b_1 and t_1 being constants independent of the length, breadth and thickness of the fuse, and κ being a constant dependent upon its
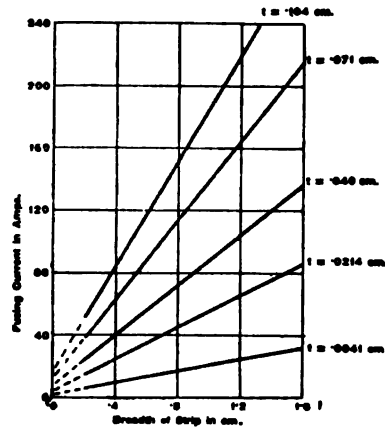
Fig. 33.—Curves connecting Fusing Current and Breadth of Strip for various thicknesses.—Zinc.

length. For zinc strip the values of the constants b_1 and t_1 can be determined from Figs. 33 and 34.

In centimetre measure $b_1 = \cdot 1$, $t_1 = \cdot 01$.
In inch measure $b_1 = \cdot 04$, $t_1 = \cdot 004$.

In Fig. 35 curves are given connecting the constant κ with the length (κ being in inch measure) for zinc strips in a vertical or horizontal position (κ in inch measure = κ in centimetre measure × 6·45).
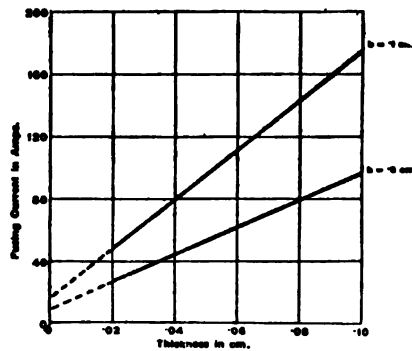
Fig. 34.—Curves connecting Fusing Current and Thickness of Strip for different breadths.—Zinc.

99

The law indicated above will hold between the following limits :—

$$\text{Thicknesses} \begin{cases} \text{·01 cm. to ·1 cm.} \\ \text{·004 in. to ·04 in.} \end{cases}$$

$$\text{Breadths} \begin{cases} \text{·4 cm. to 1·5 cm.} \\ \text{·16 in. to ·6 in.} \end{cases}$$

In these experiments the authors did not go beyond 300 amperes on a single strip, but it is probable that by using strips of increased breadth the law would hold good up to 400 or 500 amperes per strip. For fuses of large capacity it is advisable to use a number of strips in parallel, and to keep the current per strip as low as possible; by making the spacing between the strips liberal, the dissipation of the heat will be facilitated. Zinc fuses show very little deterioration even when run continuously at 90 per cent., or even 95 per cent. of
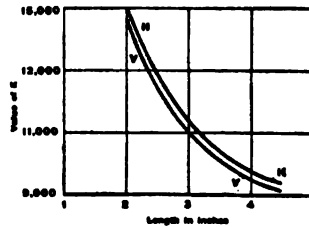
Fig. 35.—Curve connecting the Constant K in the Formula—

$$c = K \, (b + b_1) \, (t + t_1)$$

with the length of fuse.

H = Zinc strip horizontal.
V = Zinc strip vertical.

their normal fusing current; the oxidation is very slight, and the final resistance of the strip is practically the same as its initial resistance. The metal does not appear to be held up on fusion to any appreciable extent by the skin of oxide. It would be of interest to

Fig. 36.

learn from any of our readers who have had zinc fuses operating under service conditions for any length of time, whether they have observed any deterioration due to molecular change or crystallisation taking place in the strip. This freedom from oxidation when run at high current density renders zinc a desirable material for fuses which

are required to blow with only a slight overload. For circuit fuses of several hundred amperes it is not necessary or desirable that the fuse should be set for as much as 100 per cent. excess current, and in this case zinc possesses considerable advantages over copper, in that the latter becomes red-hot with about 75 per cent. of its normal fusing current, and above this point oxidises rapidly, whereas zinc only attains red heat just below fusion. It must be borne in mind, however, that for a given fusing current the mass of a zinc fuse is about 3·5 times that of a copper one of the same length, while its volume is approximately 4·4 times that of the copper, and this gives a larger amount of metal to be disrupted. Although zinc does not attain so high a temperature on fusion as copper does, yet its greater mass and volume operate unfavourably in connection with its behaviour on short circuit, and this defect is further aggravated by the fact that in open type fuses the metal is disrupted in the form of globules, which are not only red-hot but which *continue to burn* in air, and which are accompanied by dense white fumes, which deposit heavily on contiguous surfaces. For the above reasons, zinc when employed in enclosed fuse-holders would require a larger cartridge than copper, if we considered only the damage likely to arise to the case and disregarded the question of cooling.

Mr. William Cramp, a few years ago, in some hitherto unpublished experiments on fuses carried out at the Central Technical College, London, found with strip fuses of thin tinfoil which were reduced in breadth at the centre for a short distance of their length, that the length of wire disrupted on short-circuit was confined to the section with reduced breadth, and that the arc did not extend beyond this length toward the terminals. It appeared to the authors that this might be due to the cooling effect on the arc where the section of the fuse was increased, and zinc, owing to its comparatively low melting point, and the large section necessary, seemed likely to show the same effect. A zinc strip with a normal fusing current of 100 amperes was, therefore, put directly across a 100-kw. 200-volt generator, with the result that a strip of uniform width throughout was disrupted from terminal to terminal along its whole length, even with lengths of as much as 7in.; whereas when the end portions of the fuse had a greater breadth than the middle, as shown in Fig. 36A or 36B, the narrower portion only was disrupted, provided that it was about 1½ or 2 inches in length. In the early days, when soft alloys were used chiefly for fuse metal, fuses were often shaped with expanded ends (as Fig. 36A) to give larger contact area under the screw terminals. It is curious to reflect that this practice was given up in favour of using the fuse strip of uniform breadth throughout its length and soldering it to copper lugs in order to avoid the supposed danger of pinching the soft metal under the screws and thus affecting the

the fusing current, while we have thereby apparently facilitated the extension of the arc from terminal to terminal.

A further series of experiments was made with aluminium fuses in a horizontal position with the axis of breadth parallel to the ground. On plotting fusing current and breadth for a constant thickness a straight line was obtained, and the law connecting these two quantities is of the character $c \propto (b + b_1)$; $c =$ normal fusing current, $b =$ breadth, $b_1 =$ a constant.
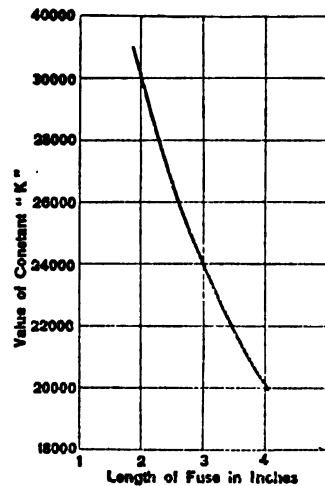
Fig. 37.

On plotting fusing current and thickness for a constant breadth a curve is obtained, which approximates to a straight line with a slight tendency to become concave towards the axis of thickness; on drawing the mean straight line, however, the deviation of the extreme points will be found not to be large, and consequently we may take it that :—$c \propto (t + t_1)$, where $t =$ thickness, and $t_1 =$ a constant. On experimenting with strip of various lengths and in different positions it was found possible to assume b_1 and t_1 constant for all cases; consequently for aluminium strip—

$$c = k \ (b + b_1) \ (t + t_1).$$

$c =$ normal fusing current; $b_1 = \cdot 035$ in inch measure $= \cdot 09$ in cm. measure; $t_1 = \cdot 0024$ in inch measure $= \cdot 006$ in cm. measure; $k =$ a constant. This law holds between the following limits :—Breadth $\cdot 15$ to $\cdot 8$ in. (probably more); thickness $\cdot 003$ to $\cdot 035$ in.; current per strip 25 to 600 amperes. The value of the constant k depends upon the position and environment of the strip and its length between

terminals, and also on the mass and character of the terminals used. The curve in Fig. 37 gives the connection between the value of the constant k in inch measure (k in inch measure = k in cm. measure × 6·45) and the clear length of the fuse between terminals, with the fuse horizontal, the axis of breadth parallel to the ground, and terminals weighing 870 grammes each. If the strip is placed horizontally, but with its axis of breadth vertical, the fusing current will be higher than that indicated by the above law, due to the greater facility for cooling due to the edgewise position. The exact amount of this increase is difficult to ascertain, as it depends upon the breadth and thickness of the strip employed; as an average value we may take the increase in the fusing current to be about 6 per cent. If the axis of length of the strip is vertical and that of breadth horizontal, the fusing current is approximately the same as when horizontal and edgewise, and thus is about 6 per cent. higher than with the strip horizontal and broadways on; in this respect aluminium differs from copper and zinc, for which the reverse holds good. Aluminium attains a dull red heat just before fusion, and a strip which will carry two or three hundred amperes will, if blown on a low-pressure circuit of 10 or 20 volts, throw off burning globules of metal to a distance of 2 or 3 feet. An examination of the fuse after rupture discloses traces of a thin oxide film, but, with the exception of strip of small dimensions, this does not seem to have a prejudicial

I—II, Zinc-Cadmium; I—III, Zinc-Tin; III—IV, Tin-Lead.
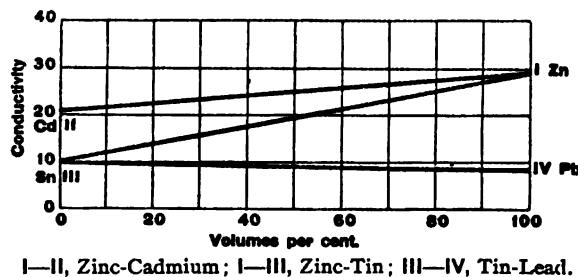
Fig. 38.

effect as regards the constancy of the fusing current. The short-circuit tests on aluminium strip were carried out on a 100-kw. generator with about twelve yards of cable of one square inch cross-sectional area in circuit. Strip with a normal fusing current of 100 amperes, when short-circuited, produced heavy fumes, and threw off numerous burning globules of metal to a distance of 15 or 20 feet. With large fuses in which the breadth has been cut down for a couple of inches at the centre, the portion disrupted is almost entirely limited to this length, but the cutting down has to be carried

to a much greater extent than with zinc. This is due probably to the much higher temperature attained by aluminium before fusion, and to the smaller volume of metal required for a given service.
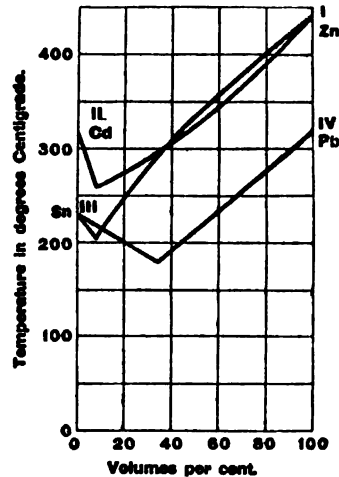
I—II, Zinc-Cadmium; I—III, Zinc-Tin; III—IV, Tin-Lead.

Fig. 39.

Unfortunately, aluminium, zinc and cadmium are highly electro-positive to copper or brass, and in the presence of moisture this contact difference of potential is likely to give rise to corrosion of the contacts, with consequent increase of contact resistance and impairment of the fuse. There are, no doubt, situations in which these metals may be employed with advantage, but for damp situations such as network boxes and section pillars, they require careful inspection and attention. Aluminium is particularly difficult to deal with in this respect, as, although in normal salt solution or normal solution of sulphuric acid it is not so electro-positive to copper as zinc is, yet unlike the latter it cannot be soldered to contact pieces or electro-plated. A good plan to adopt to overcome this difficulty would appear to be to coat the contact clips of the fuse blocks with tin, and so reduce the contact difference of potential between the fuse strip and the clips. Professor W. W. Haldane Gee has determined a number of these contact differences of potential, and his results are embodied in the following table :—

Average Electromotive Forces in volts against Sheet Aluminium at 15° C. of Commercial Samples of Metals.

—	Normal solution of common salt.	Electrolyte normal solution of sulphuric acid.	Normal solution of caustic soda.
Copper	− 0·54	− 0·49	− 1·23
Zinc	+ 0·31	+ 0·47	− 0·29
Tin	− 0·35	+ 0·08	− 0·44
Iron	− 0·33	− 0·11	− 0·90
Nickel	− 0·50	− 0·35	− 0·94
Carbon	− 0·80	− 0·63	− 1·15
Brass	− 0·43	− 0·50	− 1·18
Silver	− 0·57	− 0·47	− 1·16
Cadmium	+ 0·032	+ 0·41	− 0·57

It may not be without interest at this juncture to contrast the conductivity of various alloys of the metals under consideration, and also their melting points. Fig. 38 shows graphically the results obtained by Mathiessen for the conductivity of alloys of cadmium-zinc, tin-zinc, and tin-lead of varying proportions by volume. Fig. 39 shows the melting points of these alloys in degrees Centigrade plotted from Gautier's determinations. Some of the zinc-aluminium alloys are already in use for fuses.

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APPENDIX.

TABLE OF CONSTANTS.

For use with the authors' formula $C = Ad^n$ for determining the fusing current of wires under various conditions and for diameters measured in inches, centimetres, or millimetres, together with the nearest sizes on the Standard Wire Gauge. Wire free in air from terminal to terminal in all cases.

Particulars of Fuse.	Range on S.W.G.	Range of Fusing Currents.	Index.	Constant. Cms.	Inches.	mm.
TINNED COPPER:—Lengths of 2 inches and upwards, Horizontal......	47 to 33	1 to 10	1·195	821·3	2,501	52·4
Lengths of 6 inches and upwards, Horizontal	33 „ 18	10 „ 100	1·403	1,768	6,537	69·9
„ 2 „ „ Vertical	47 „ 33	1 „ 10	1·195	775	2,360	49·4
„ 6 „ „ Vertical	33 „ 18	10 „ 100	1·403	1,680	6,220	66·6
Length of 4 inches, Horizontal, with large terminals	33 „ 18	10 „ 100	1·586	2,980	13,100	77·5
„ 4 „ Vertical	33 „ 18	10 „ 100	1·586	2,844	12,470	73·8
„ 1½ „ Horizontal, with small terminals	47 „ 33	1 „ 10	1·264	1,178	3,828	64·1
„ 1½ „ Vertical	47 „ 33	1 „ 10	1·264	1,112	3,611	60·5
„ 1½ „ large terminals	47 „ 33	1 „ 10	1·34	1,690	5,890	77·3
„ 1 inch, Horizontal, with small terminals	47 „ 33	1 „ 10	1·32	1,567	5,360	75
„ 1 „ Vertical	47 „ 33	1 „ 10	1·32	1,480	5,060	70·8
„ 4 inches, Vertical in Manchester Corporation House Service Box, with cover on mass of terminals, about 100 grms	33 „ 18	10 „ 100	1·614	3,228	14,530	78·5
TIN:—Lengths of 3 inches and upwards, Horizontal	43 „ 20	1 „ 10	1·131	146·6	420·6	10·84
Ditto, lengths of 6 inches and upwards, Horizontal	20 „ 7	10 „ 80	1·32	239·3	819	11·46
SILVER:—Lengths of 5 inches and upwards, Horizontal	35 „ 18	7 „ 70	1·287	967	3,210	50
ALUMINIUM:—Length of 4 inches and upwards, Horizontal	42 „ 22	3 „ 45	1·461	2,188	8,539	75·7
Ditto for critical currents, with spring attachment	42 „ 20	2 „ 30	1·271	640	2,091	34·3

The Use of Balanced Electrodes.

By Professor W. W. HALDANE GEE, B.Sc.

THE weight voltameter furnishes us with a very accurate method for the determination of current strength, but its use requires care and time. In the case, for example, of the silver voltameter according to the Board of Trade directions,* the deposited silver must be washed with distilled water and left to soak for *at least six hours*, and then washed and dried in a hot-air bath. Every determination involves a repetition of these and other lengthy processes. In seeking for a more ready method of working, which at the same time should be sufficiently accurate for commercial purposes and give facility in making repeated measurements, I have been led to consider the use of the hydrostatic balance. This method was adopted by Roseleur for the purpose of the electroplater. When the weight of the suspended cathode reached a certain amount the balance beam tilted over, and at the same time broke the electrical circuit through the plating bath. Pfanhauser† has recently designed a more convenient instrument in which an electric bell is rung when the required quantity of silver has been plated out. The coulombmeters of Edison and Long-Schattner are attempts to apply the hydrostatic method to the measurement of electric supply. Occasional use has been made of the method in the lecture room, as in Langley's experiment,‡ to show that the weight of a copper electrode increases or decreases according as it is cathode or anode, but I have been unable to find any mention of the method in use in the laboratory or the testing-room. Moreover, in the cases cited either a special balance has been used or the electric current has been taken through the moving parts by mercury cups, flexible connections, or knife edges. My aim has been to make use of any ordinary physical balance, which, as a rule, possesses agate knife edges resting on agate planes. I have found an Oertling 16-inch beam balance very convenient for the purpose, and its use will now be described. A hole about an inch in diameter is cut under the centre of the right-hand pan (see Fig. 1). A corresponding hole is drilled in the bench on which the balance is placed—this is not shown in the figure. The right-hand pan is removed and a smaller pan p from a cheap balance is substituted. This is used like the so-called specific-gravity pan with which balances are sometimes provided. Suspended from a hook at the bottom of the pan is a fine copper wire w, which should be varnished at its lower end. At c is a piece of copper wire twisted round the vertical wire. This is for the purpose of making connections. The cathode C has been usually of cylindrical shape, with three wires riveted across the top. At the junction of the three

* *London Gazette*, August 24, 1894.
† *Zeit. f. Elektro-chem.* October 10, 1904.
‡ *Zeit. phys. Chem.* 2. 83-91 (1881).

cross-wires the fine suspension wire is fastened. The anode A has also usually been of cylindrical form. The clean cathode having been suspended in the electrolyte, is counterpoised (the wire at c being disconnected from the circuit). Next, a series circuit is made up of an ammeter, a rheostat, a key, the voltameter and a source of low
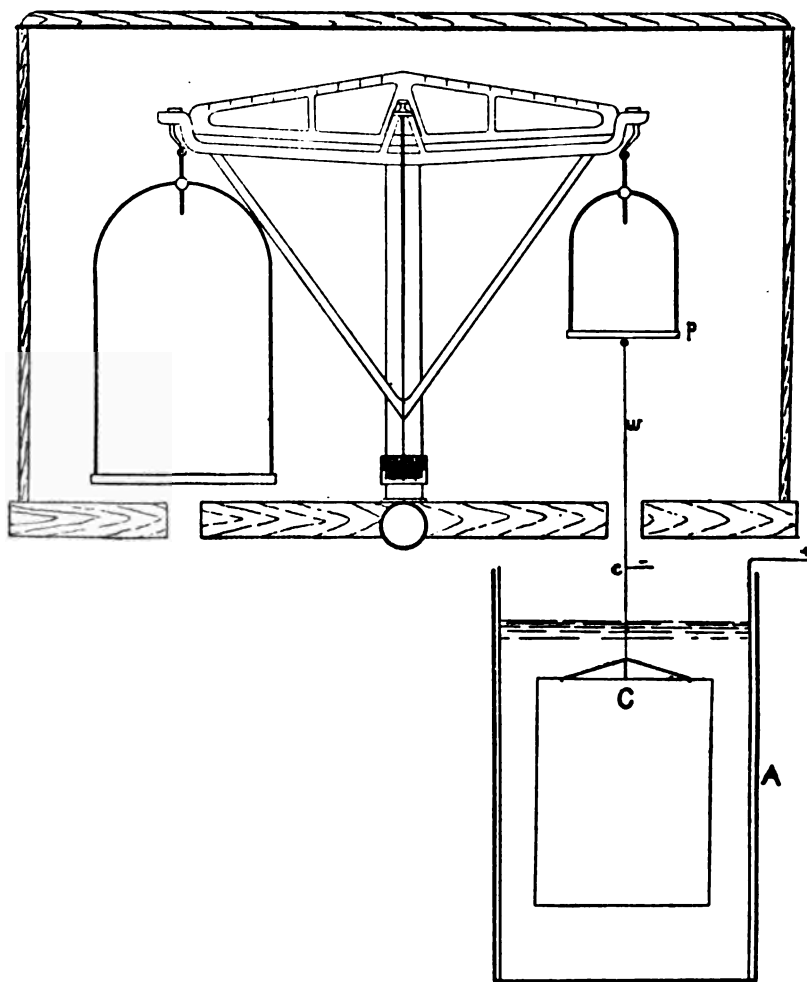
Fig. 1.

voltage supply. The current is passed for a definite time, the rheostat being adjusted as necessary so as to keep it constant. When the amount of deposit is deemed sufficient the current is stopped and the connection at c removed; the liquid should now be gently stirred and then the gain in weight ascertained by an accurate set of weights (a 100-gram set of platinised weights by Kuhlmann was found very useful for this purpose). The density of the solution is then found by a specific gravity balance or hydrometer. The method of calculation to find the current strength from the gain in weight and the time of deposit is as follows :—

Let V = volume of the deposited metal,

Δ = its density,

δ = the density of the liquid,

M = real mass of the deposited metal,

m = apparent mass of the deposited metal,

C = current strength in amperes,

t = time of current passing in seconds,

z = electro-chemical equivalent of the deposited metal.

then we have

$$V\Delta = M$$
$$V\Delta - V\delta = m$$

hence

$$M - \frac{\delta M}{\Delta} = m$$

or

$$M = \frac{\Delta}{\Delta - \delta} \times Ctz,$$

therefore

$$C = \frac{\Delta}{\Delta - \delta} \times \frac{m}{tz} = \frac{km}{tz}.$$

If an error be made in fixing the density Δ of the metal, then since this quantity occurs both in the numerator and the denominator, the effect on the constant k and the result will be relatively small. Thus if δ be nearly unity and an error a be made in the value of Δ then

$$k = \frac{\Delta}{\Delta - 1},$$

and $$k_1 = \frac{\Delta + a}{\Delta + a - 1},$$

or the percentage error in the multiplying factor will be

$$\frac{k_1-k}{k}\times 100 = \frac{\dfrac{\Delta+a}{\Delta+a-1}-\dfrac{\Delta}{\Delta-1}}{\dfrac{\Delta}{\Delta-1}}\times 100$$

$$= \frac{100a}{\Delta(\Delta-1)}\text{nearly.}$$

Thus in the case of copper, if instead of 8·9 the actual density were 9·0, then

$$\frac{100\times 0\cdot 1}{8\cdot 9\ \times 7\cdot 9}=0\cdot 1423\text{ per cent.};$$

or, again, if we take the case when Δ might be either 8·8, 8·9, or 9, and the value of $\delta= 1\cdot 15$,

$$\frac{8\cdot 8}{8\cdot 8-1\cdot 15}=1\cdot 150$$

$$\frac{8\cdot 9}{8\cdot 9-1\cdot 15}=1\cdot 148$$

$$\frac{9}{9-1\cdot 15}=1\cdot 147$$

or the percentage error between the extreme values is

$$\frac{(1\cdot 150-1\cdot 147)\ 100}{1\cdot 147}=0\cdot 26,$$

therefore an error in fixing Δ will be much less than is likely to occur in the best of commercial ammeters or coulombmeters. I have so far chiefly used the method in the case of copper deposition from a sulphate bath, and in fixing on a number for the density of electrolytic copper have compared the densities given by different authorities with my own experiments, and conclude that it will be sufficiently correct to assume for electrolytic copper a density of 8·9. The following tables, Nos. I., II., and III., give the results of a number of experiments. In these tests it was necessary to keep the current, observed by various types of laboratory ammeters, constant throughout the run. This requires repeated adjustment of the rheostat, hence the results depend on the watchfulness of the observer and the care of his adjustments. A much more rigorous test is to use an ordinary weight voltameter in series with the suspended electrodes. The results of tests made in this way will be given in a later table.

TABLE I.—ELECTROLYSIS OF COPPER SULPHATE SOLUTION.

No. of Experiment.	1	2	3	4	5	6	7
Apparent Weight of Deposit in grams	0·249	1·27	1·115	0·647	5·90	5·39	30·4
Time of Deposit in secs.	1,380	4,680	1,800	2,400	3,600	7,680	3,600
Density of Solution	1·05	1·05	1·05	1·05	1·01	1·20	1·20
Calculated amperes	0·622	0·935	2·13	0·929	5·62	2·465	29·67
Observed amperes	0·620	0·935	2·11	0·930	5·58	2·50	30·00

The current density was kept under $\frac{1}{10}$ ampere per square inch. Electro-chemical equivalent $= 0·000329$.

TABLE II.—ELECTROLYSIS OF ZINC SULPHATE SOLUTION.

No. of Experiment.	1	2	3
Apparent Weight of Deposit in grams	0·512	1·316	2·030
Time of Deposit in seconds	2,520	6,600	10,200
Density of Solution	1·05	1·05	1·05
Calculated amperes	0·707	0·694	0·692
Observed amperes	0·700	0·688	0·703

The current density was 0·06 ampere per square inch. Density of electrolytic zinc taken as 6·9. Electro-chemical equivalent $= 0·000339$.

TABLE III.—ELECTROLYSIS OF SILVER NITRATE SOLUTION.

No. of Experiment.	1	2	3	4
Apparent Weight of Deposit in grams	1·895	4·826	1·694	1·952
Time of Deposit in seconds	3,780	5,040	1,680	1,920
Density of Solution	1·15	1·15	1·15	1·15
Calculated amperes	0·504	0·968	1·020	1·028
Observed amperes	0·500	0·960	1·000	1·000

Density of silver $= 10·4$. Electro-chemical equivalent $= 0·001118$.

Use of Two Balanced Electrodes. It will evidently be possible to have two depositing experiments going on at one time by making use of both sides of the balance. The best manner of doing this was found to be as follows : Two specific-gravity pans have been used, one for each side of the balance, and the suspending wire has on each side been supported by a loop of silk, so as to avoid any short circuits through the balance. The wire on the left-hand pan being unhooked, the right-hand electrode is balanced by weights in the left-hand pan. Next, the right-hand loop is unhooked and that on the left-hand side is replaced. Now the left-hand electrode is balanced by the addition of weights to the right-hand pan. The two voltameters are now run in series, taking care that the suspended electrodes are both cathodes. At the termination of the experiment the above system of independent weighing is repeated so as to obtain in each case the amount of deposit. As an example will be given the

determination of the ratio of the electro-chemical equivalents of copper in the form of cupric sulphate, and of copper in the case of a commercial cyanide bath. This latter was made according to the old method of Watt. Since the same number of coulombs Q pass, we have here—

$$M = Qz = \frac{\Delta m}{\Delta - \delta} \text{ for the sulphate,}$$

and

$$M_1 = Qz_1 = \frac{\Delta m_1}{\Delta - \delta_1} \text{ for the cyanide,}$$

or

$$\frac{z}{z_1} = \frac{\Delta - \delta_1}{\Delta - \delta} \cdot \frac{m}{m_1}.$$

In an experiment the following values were found :—

$$m = 4{\cdot}82 \qquad \delta = 1{\cdot}11$$
$$m_1 = 9{\cdot}72 \qquad \delta_1 = 1{\cdot}12$$

which gives $z_1/z = 2{\cdot}025.$

This confirms the interesting fact that in the cyanide solution the copper acts as a monad.

Electrolysis of Mercury Compounds with Mercuric Electrodes. A further example of the utility of the method of double weighings is in the investigation of the electrolysis of mercury salts with mercury electrodes. Here the use of suspended electrodes is peculiarly adaptable. The apparatus designed for the purpose is shown in Fig. 2. A glass vessel was provided with a layer of mercury A at the bottom to serve as an anode, whilst a glass dish *g* (made by cutting off the neck of a bottle) was suspended from an inverted U of glass rod *r*, having its ends pushed into two holes in a cork *c*. The suspending wire *p* was of platinum. Connections were made to the electrodes by glass tubes *t* and *t₁*, with short lengths of platinum wire fused through the ends; the tubes contain mercury in which amalgamated copper wires *w* and *w* are inserted. The first experiments were made with solutions of mercurous nitrate acidified with nitric acid. This mercury voltameter was run in series with a suspended electrode copper voltameter. The copper sulphate solution used contained ethyl alcohol according to the advice of Oettel. When the circuit was completed electrolytic vibrations were set up, such as have been described by Gore and others, and when the current density was increased basic salts were formed both at the mercury anode and cathode, and crackling sounds were produced. By diminishing the current density the electrolysis seemed to proceed in
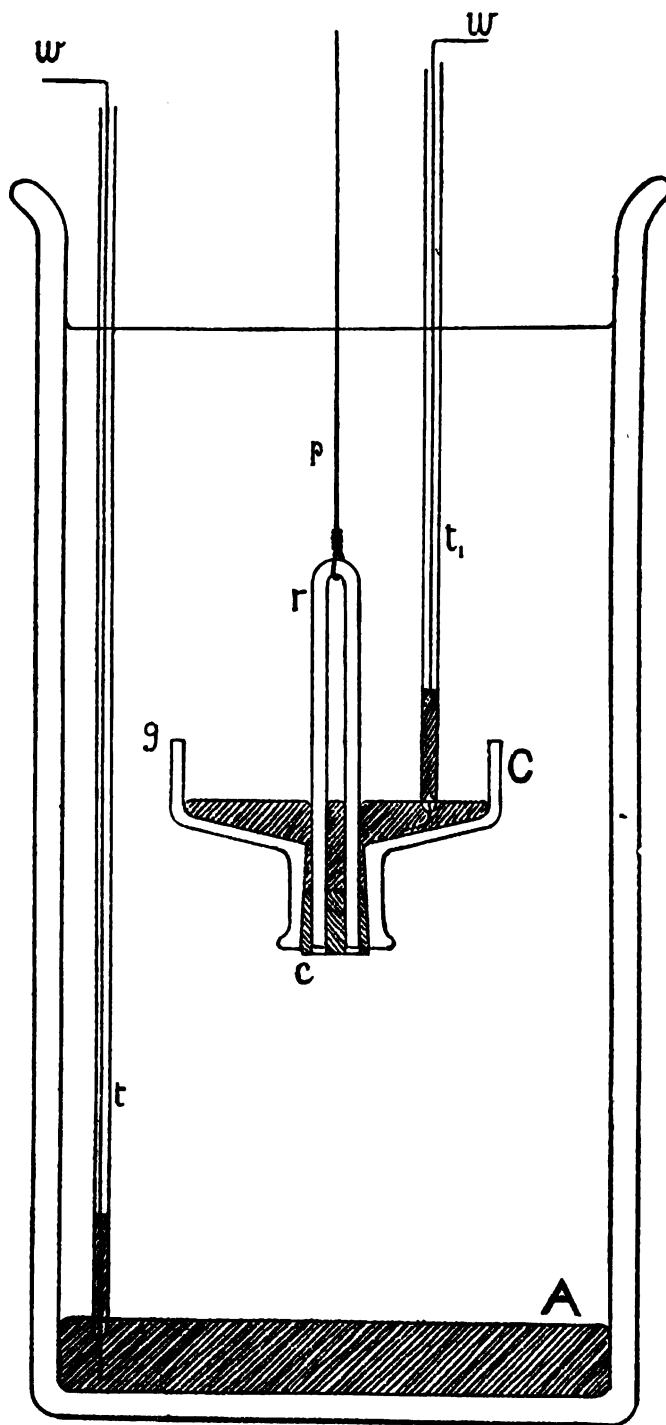
Fig. 2.

a normal manner with little effect on the surfaces of the mercury, any slight film of basic salt on the cathode being redissolved on agitating the liquid. The following results were obtained :—

TABLE IV.—ELECTROLYSIS OF MERCUROUS NITRATE.

No. of Experiment.	1		2		3
Gain of Hg cathode	1·86	......	11·85	......	10·54
„ Cu „	0·29	......	2·13	......	1·73
Density of Hg solution	1·07	......	1·07	......	1·07
„ Cu „	1·128	......	1·13	......	1·13
Time in seconds	5,400	......	5,400	......	6,000
Current by ammeter	0·180	......	1·400	......	1·000
Current calculated from Cu	0·187	......	1·374	......	1·003
Ratio of Hg to Cu equivalents	6·078	......	5·272	......	5·775
Current efficiency of Hg, per cent.	96·6	......	83·8	......	91·8

Using the equivalents of the International Committee of 1903, $Hg^{\cdot}=198\cdot50$ and $Cu^{\cdot\cdot}=31\cdot55$, giving a ratio of $Hg/Cu=6\cdot291$. These results showing a relatively poor current efficiency, probably due to the presence of mercuric salts, it was thought that better results would be obtained by the use of the solutions that have been found satisfactory in electro-chemical analysis. A solution containing 100 grms. of $HgCl_2$, 300 grms. of KCN, and 3·8 litres of water was made up, and the same apparatus used as last described. An additional check was obtained on the results by weighing the copper cathode clean and dry before commencing the experiment, and again after the deposition it was washed, dried, and weighed. Table V. gives some of the results.

TABLE V.—ELECTROLYSIS OF $HgCl_2$ MIXED WITH KCN.

No. of Experiment.	1		2		3
Apparent gain of Hg	4·08	......	5·31	......	5·15
„ „ Cu	1·25	......	1·63	......	1·55
Real gain of Cu	1·43	......	1·85	......	1·81
Density of Cu solution	1·13	......	1·13	......	1·132
„ Hg „	1·08	......	1·08	......	1·134
Time in seconds	10,800	......	10,800	......	14,400
Current by ammeter	0·400	......	0·500	......	0·300
Current calculated from real gain of Cu	0·402	......	0·521	......	0·3820
„ „ apparent gain of Cu	0·403	......	0·526	......	0·3748
„ „ „ „ Hg	0·395	......	0·514	......	0·3785
Ratio of equivalents of Hg/Cu by experiment	3·095	......	3·118	......	3·103
Percentage current efficiency of Hg	98·5	......	99·3	......	98·7
Current density at Hg cathode, amps. per sq. in.	0·13	......	0·16	......	0·10

Voltage between Hg electrodes was from 2-3. The ratio of $Hg^{\cdot\cdot}$ to $Cu^{\cdot\cdot}$ is taken as 3·145. The electrolytic vibrations were well marked
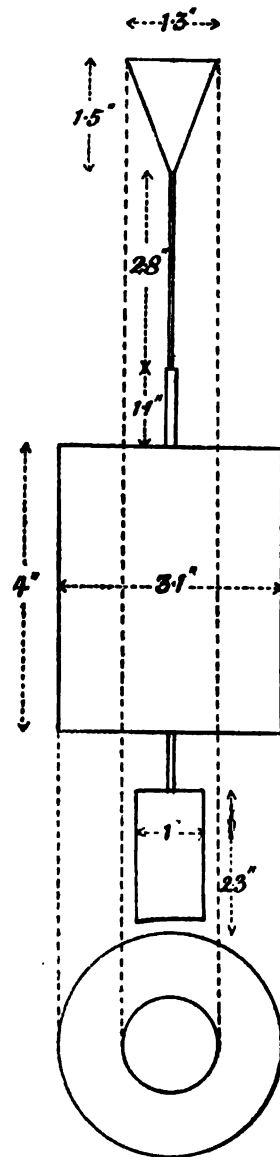
Fig. 3.

at the cathode, and gave rise to very curious appearances on the surface of the mercury.

Comparison of Weight Voltameters. Two identical copper voltameters were fitted up, and the vessels were filled with a 15 per cent. solution of copper sulphate crystals made slightly acid with sulphuric acid. Both sides of the balance were used. The cathodes were weighed dry and then suspended in the solutions and balanced against each other and also separately weighed. They then were connected in series, but no care was taken to keep the current constant. After deposition they were again balanced against each other, again separately weighed in the solution. Next they were removed from the solution, well washed, dried, and finally weighed.

TABLE VI.—COMPARISON OF VOLTAMETERS (Δ TAKEN AS 8·95).

Experiment	1	2	3	4	5
Gain of right-hand cathode in air (a)	2·446	13·842	10·511	30·354	12·252
Gain of left-hand cathode in air (b)	—	13·876	10·446	30·320	12·254
Gain of right-hand cathode in $CuSO_4$ (c)	2·172	12·281	9·337	26·946	10·896
Gain of left-hand cathode in $CuSO_4$ (d)	—	12·313	9·316	26·860	10·858
Time in seconds	7,200	21,600	16,800	69,120	30,600
Current in amps. at start (about)	1·0	2·0	2·0	2·0	2·0
Density of solutions	1·05	1·048	1·048	1·045	1·045
Current density, amperes per square inch (about)	0·03	0·06	0·06	0·06	0·06
Real gain of right-hand cathode calculated from (c)	2·461	13·91	10·57	30·49	12·33
Real gain of left-hand cathode calculated from (d)	—	13·94	10·54	30·41	12·27
Percentage difference of mean of (c) & (d), & mean of (a) & (b)	0·41	0·051	0·45	0·40	0·38

These results show that the method of suspended electrodes is trustworthy to about one-half per cent.

Hydrometer Method. It was thought that the use of a hydrometer made of thin brass (exactly like the old Nicholson's hydrometer) as a combined cathode and balance would furnish an instructive instrument that in certain cases might be useful. The dimensions of the instrument made for this purpose are shown in Fig. 3. The method of arranging the connections was as in Fig. 4. It was found very convenient to keep the hydrometer C always in circuit. This was done by the use of two very flexible leads X, which were con-

B

R

H

H,

S

P

X

X

W

A

A

C

H
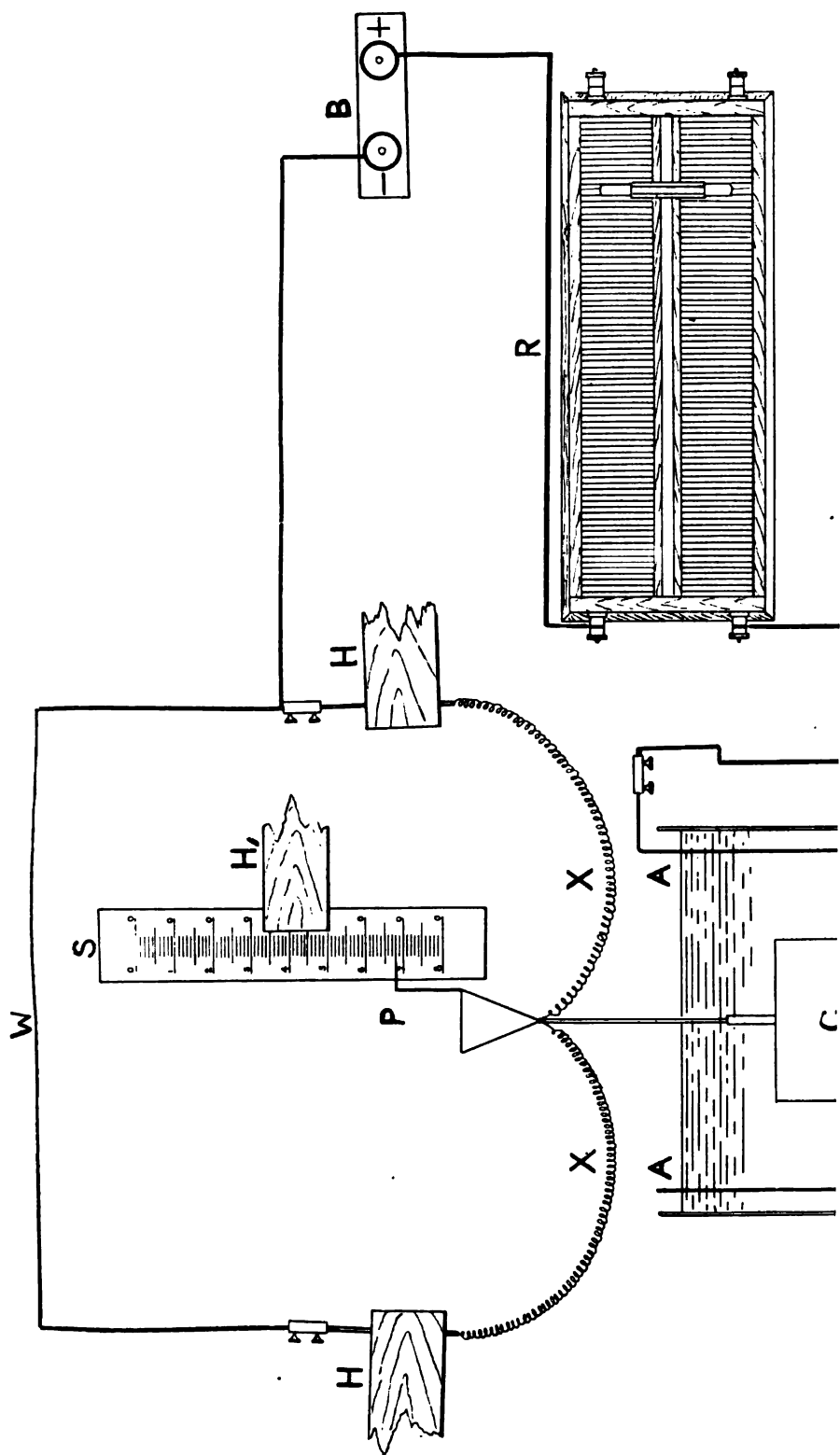
nected in parallel by the wire W. The ends of these wires were supported by wooden clamps H and H. The position of the hydrometer was observed by the help of the pointer P that moved in front of the millimetre scale S etched on mirror glass, supported by the wooden clamp H_1. A low-voltage supply B was in series with the rheostat R, the ammeter M and the circular copper anode A. The usual solution of copper sulphate was employed. When the hydrometer weight had been adjusted so that it floated out of the liquid at a convenient height, then a weight was placed in the cup and the position of P noted on the scale. The weight was then removed from the cup and current passed until P again reached the noted position. Calling V the volume of the hydrometer up to the index mark, δ the density of the electrolyte, M the mass of the hydrometer, x the increase in volume of the instrument due to the deposited metal, μ the mass of the deposited copper, and m the standard weight placed in the cup. Then—

$$V\delta = M$$
$$(V+x)\delta = M+\mu-m$$
$$\mu = \Delta x$$

hence

$$\mu = \frac{m\Delta}{\Delta-\delta}$$

giving the same formula as in the case of the balance.

Example. A current of 2 amperes as observed on a rough ammeter was found necessary to deposit 0·5 grm. in 14 minutes; hence the calculated current is

$$\frac{8·9}{8·9-1·16} \times \frac{·5}{60 \times 14 \times ·000329} = 2·08$$

1·16 being the density of the electrolyte. The method is quite workable, but is rather troublesome as compared with the use of a balance, and cannot be as accurate.

Use of Spring Balance. An arrangement similar to Jolly's balance can also be adopted. A long spring of fine steel wire Sp (see Fig. 5) supports a balance pan and a cylindrical cathode C. The electrical connections can be arranged as with the hydrometer. In either case it is convenient to have a commutor in the circuit, enabling the deposited metal to be removed and the zero point of the instrument, given by the position of P on the scale S, adjusted.

Example. The addition of 0·5 grm. to the scale moved the pointer 13 mm. The weight was removed and a current passed for fifteen

minutes, when the pointer sank 6 mm. Hence the apparent weight of the deposit is o·231 grm., and the calculated current is

$$\frac{8 \cdot 9}{8 \cdot 9 - 1 \cdot 06} \times \frac{0 \cdot 231}{60 \times 15 \times 0 \cdot 000329} = 0 \cdot 89 \text{ amperes,}$$

the density of the electrolyte being 1·06. A more accurate method will be to use a reading telescope in the following way : A known weight is added to the scale-pan, and the position of an indicating mark on the bottom of the spring is observed through the telescope. The weight was then removed and the current passed until sufficient metal was deposited to bring the index mark again to its former position.

EXAMPLES.

Experiment	Density of Solution.	Apparent Weight.	Time (seconds).	Current by ammeter (amperes).	Current calculated (amperes).
1	1·12	0·4	2,470	0·60	0·56
2	1·12	0·2	1,475	0·50	0·47
3	1·12	0·2	1,460	0·50	0·48
4	1·12	0·3	1,795	0·60	0·58

With the use of a suitable shunt the spring balance with scale may be converted into a laboratory type of coulombmeter.

Use in Density Determinations. There is undoubtedly some difficulty in obtaining even approximately accurate figures for the density of electro-deposited metals. When the metal is deposited on, say, black-leaded tin, from which it can be stripped and then weighed in air and water, two sources of error are introduced. Firstly, the metal is liable to oxidation, and secondly, air bubbles are introduced which are most difficult to remove even with the assistance of an air-pump. The method of suspended electrodes furnishes a means of avoiding these difficulties. If it can be assumed that the weight of the deposited metal can be ascertained by applying Faraday's law, the current being given by an accurate ammeter, then the weight M of the metal is known and the balanced electrode will give the apparent weight *m*, then

$$\Delta = \frac{M\delta}{M - m}.$$

The value of M can be ascertained with less objection by using an ordinary voltameter in series with the suspended electrode. To obtain an accurate result it is important that M−*m* should be sufficiently large so that the individual errors of M and *m* cannot exercise an important effect on their difference. This will be seen by an examination of the following example where the amount of deposit is insufficient :—

Sp

S

P

X   X

A

C
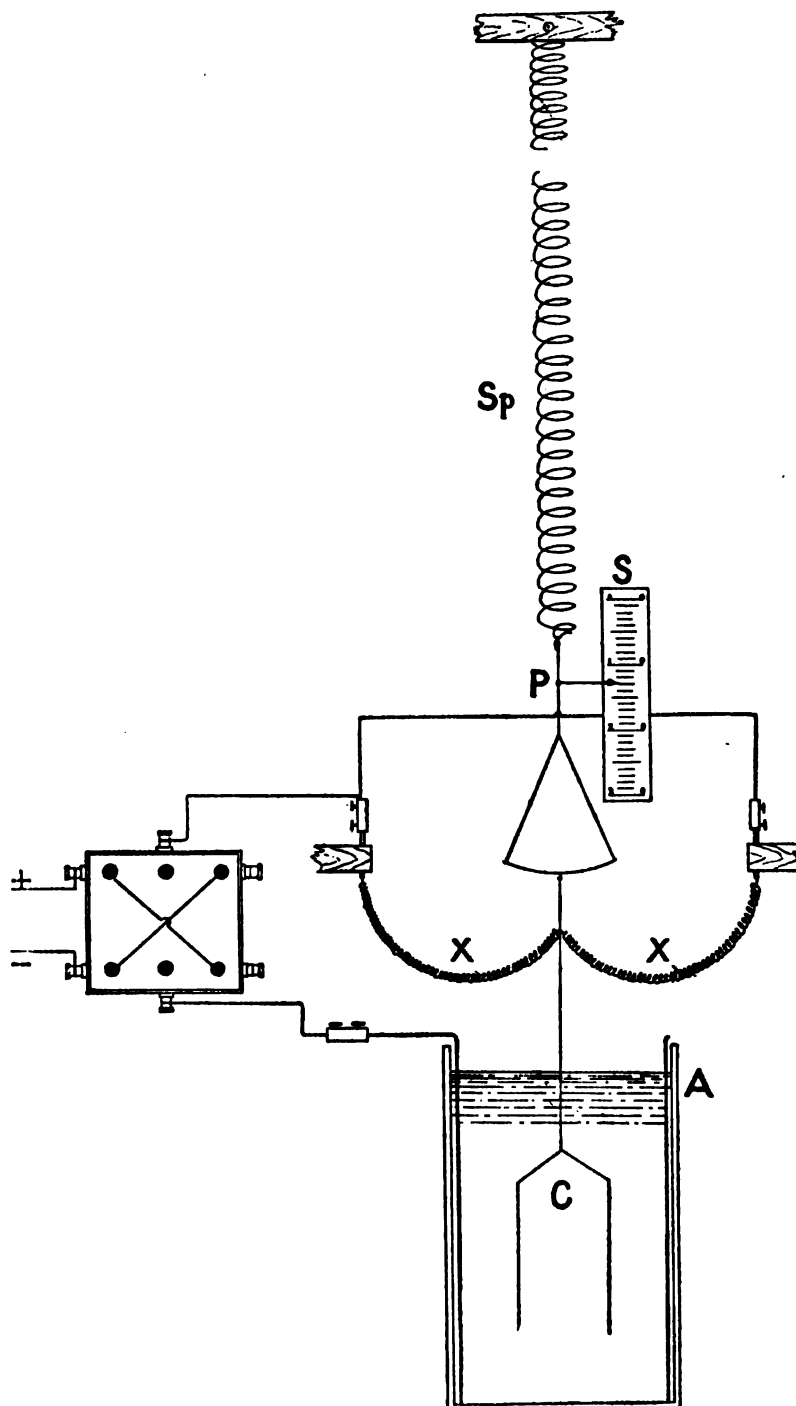
Fig. 5.

Example. By using a copper voltameter the actual weight of copper deposited in air was found to be 1·43 grm., and the apparent weight was 1·25 in a solution of density 1·13; hence

$$\Delta = \frac{1\cdot43 \times 1\cdot13}{1\cdot43 - 1\cdot25} = 8\cdot97.$$

Determinations of the density of various metals by this method are in progress.

Use of Anode and Cathode Suspended from one Balance Arm. Cylinders of copper A and B (Fig. 6), supported by fine varnished wires by the rod of metal *a b* are suspended by the silk thread *c d*, which was supported from the bottom of one of the balance pans. These cylinders were suspended centrally within two larger ones C and D and a current was passed so that A acts as a cathode and B as an anode, *a d b* acting as a connecting rod. The electrolyte in the containing vessels may be identical or different as to temperature and nature. This arrangement provides a convenient means of ascertaining whether or not the gain of A is equal to the loss of B,
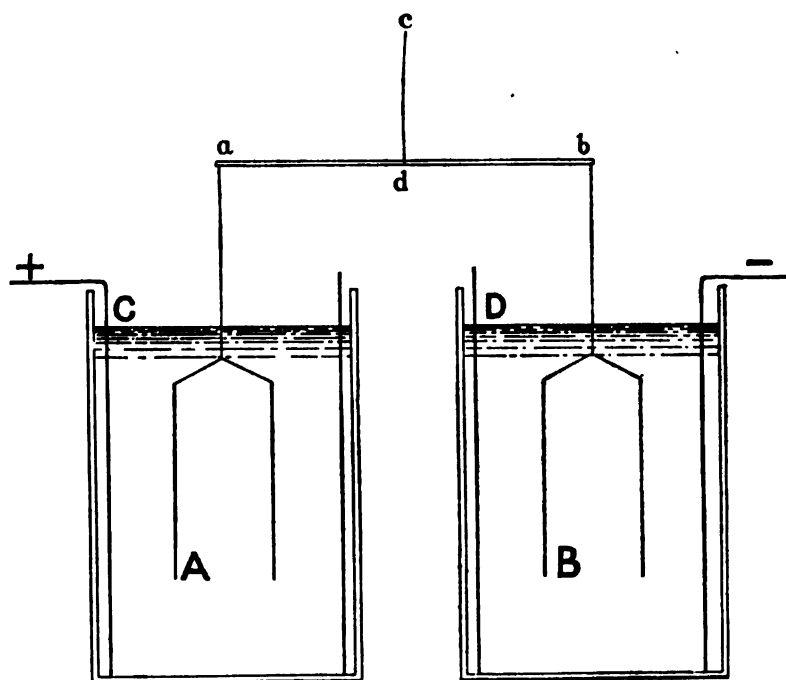
Fig. 6.

with the advantage that continual observations may be made, since no connections are made that interfere with the motion of the balance. If a sufficiently accurate ammeter be placed in the circuit, then by noting the time of deposition the gain of A can be calculated and the percentage difference between loss and gain calculated. Using solutions of copper sulphate slightly acid, each of density 1·14 and at the ordinary temperature, a number of experiments have been made.

Example. A current of 0·6 amperes was passed for ninety minutes, when the apparent loss of the electrodes was 0·014 grm.; therefore the percentage loss of weight of the anode is

$$\frac{0\cdot014 \times 8\cdot9 \times 100}{(8\cdot9-1\cdot14) \times 0\cdot6 \times 5,400 \times 0\cdot000329} = 1\cdot5.$$

Application for Large Currents. In the electro-chemical laboratory of the Manchester School of Technology is a slate tank that holds 90 gallons of copper sulphate solution. This is provided with the usual three brass rods for supporting the electrodes. A balance for rough weighings, provided by Kaehler and Martini, was mounted on a wooden plank resting on the edge of the tank so that the middle or cathode rod could be suspended from one arm of the balance. To the brass rod four cathode plates of copper were suspended by copper wires so that the cathodes were completely immersed in the electrolyte. The balancing having been completed to within a decigram a flexible lead was attached by a clamp to the middle of the bar and the current was passed. An accurate switchboard ammeter was in circuit. The current was provided by the Schuckert "electro-chemical" dynamo. This dynamo is directly driven by a 60 H.P. motor from the School electric lighting station. By the use of the shunt regulator it was found that the current could be kept quite constant. The following results were obtained :—

Experiment.	Time (minutes).	Deposit. Grams.	Current (observed). Amperes.	Current (calculated). Amperes.
1	55	189·4	200	199·9
2	45	143·0	180	180

Further experiments are in progress with the view of using this method for the verification of electric supply meters.

Use of Rough Balances. In place of either hydrometer or spring balance some form of ordinary balance is as a rule much to be preferred, and I may point out here that a balance such as is used for rough weighings to an accuracy of a centigram may be converted into a very convenient arrangement for a number of laboratory purposes. These include the determination of densities and the

coefficient of cubical expansion by the method of Matthiessen. Such a balance is specially useful in the lecture room. Two holes should be made in the base of the balance and then it should be mounted on a wooden stand with four legs (so as to raise the bottom of the balance about 12 inches above the table). Two holes are made in the top of this stand, just under the holes in the base of the balance. The ordinary pans are best replaced by two specific-gravity pans which may readily be constructed of sheet brass provided with silk cords. With a balance so fitted a course of work for elementary students has been arranged.

Conclusion. Sufficient has been done to show that the use of suspended electrodes is worthy a place amongst laboratory, test-room, and workshop methods as a means of quickly arriving at a result that is sufficiently accurate for many purposes. It enables decisions between rival methods to be settled with comparative ease. Being an indicator of coulombs, it has the advantage over the use of an ammeter which must be periodically read in order that calculations relating to quantity can be effected. A balance fitted in the way I have described should find a place in every physical and electro-mechanical laboratory.

The Lustre, the Tinctorial Properties,

and the structural alterations which result from treating cotton with mercerising & other liquids.

By Mr. JULIUS HÜBNER and Prof. W. J. POPE, F.R.S.

THE study of the action upon the cotton fibre of soda solutions of too great dilution for use in practical mercerisation must be considered a necessary preliminary step to the obtaining of information as to the changes in the fibre which are produced by mercerisation. In order to ascertain whether dilute soda solutions have any action of a chemical or morphological nature on cotton, we steeped dry hanks of twofold 50's bleached yarn in caustic soda solutions of known concentrations varying from $1°$ Tw. up to $80°$ Tw., and, after washing in cold water until all the soda was removed, dyed all the hanks, together with an untreated one for purpose of comparison, in a solution of Benzopurpurin 4 B, the amount of dye-stuff used being one quarter per cent. on the weight of the hanks. After dyeing in the boiling bath for half an hour the hanks were removed, washed, and dried; they were then matched by the eye, an attempt being made to form some quantitative appreciation of the relation between the strength of the dyeings on the different hanks. This quantitative relationship, so far as it can be established in a rough preliminary test of this character, is given in Table I., in which the letter "s" signifies "stronger than," and the letter "w" means "weaker than," the repetition of the letter indicating "much greater than" or "much weaker than," as the case may be. Assuming that, in a roughly quantitative way, the increase of strength or weakness of the dyeing is proportional to the number of repetitions of the characterising letter, it is convenient to express the results of the trial and its graphic representation in a curve as in Fig. 1.* Although we do not claim that this trial and its graphic representation by the curve have any rigidly quantitative value, yet the following points must be considered as definitely proved, namely :—

1. Cold caustic soda solution of $1°$ Tw. has a considerable effect in increasing the affinity of cotton for direct dyeing colouring matters, and, from $0°$ to about $18°$ Tw., the increase in affinity for the dyestuff is roughly proportional to the concentration of the soda used in the previous treatment of the cotton.

2. Between $18°$ to $22°$ Tw. the increase in concentration of the soda has a greater effect in increasing the affinity of the cotton for the colour than has a corresponding increase of concentration in soda of lower strength.

* In this curve we have plotted the concentration of the soda in Twaddell degrees, since the strength in degrees Twaddell is roughly proportional to the percentage concentration.

3. The effect referred to in (2) becomes greater with soda of density 22° to 26° Tw., and much greater still with soda of from 26° to 30° Tw.

4. Above 30° Tw., however, an increase in strength of the soda exerts a less effect than before in increasing the affinity of the cotton for the colour, so that raising the strength of the soda solution from 30° to 40° Tw., has only about the same effect in increasing the affinity of the fibre for colour as increasing the concentration of the soda from 26° to 28° Tw. or from 28° to 30° Tw. At above 45° Tw. increased concentration of the soda produces but little effect in heightening the shade produced on dyeing, so that practically the maximum increase in affinity for colour is got by treating with soda of any concentration between 55° and 70° Tw., and an experienced eye is needed to see that the dyeing on the hank treated with 70° Tw. soda is stronger than that on the hank treated with 55° Tw. soda.

5. As the concentration of the soda used in mercerising is increased above 70° Tw. an actual diminution in the affinity of the fibre for the dyestuff accompanies the increase in concentration; thus, the hank treated with soda of 70° Tw. dyes much more strongly than does that treated with 80° Tw. lye. This reversal of the action of the soda is of so strongly marked a character that the hank treated with soda of 80° Tw. dyes to the same shade as that treated with soda of 35° Tw.

TABLE I.—Hanks treated with various Strengths, stated in Twaddell degrees, of Soda Lye at 19°C., and afterwards dyed with ¼ per cent. of Benzopurpurin 4 B, calculated on the Weight of the Hanks.

°Tw.		°Tw.	°Tw.		°Tw.	°Tw.		°Tw.
1	2 S	0	14	2 S	12	45	2 S	40
2	2 S	1	16	2 S	14	30	s	45
3	2 S	2	18	2 S	16	55	s	50
4	2 S	3	20	3 S	18	60	s	55
5	2 S	4	22	4 S	20	65	s	60
6	2 S	5	24	6 S	22	70	s	65
7	2 S	6	26	6 S	24	75	3 w	70
8	2 S	7	28	10 S	26	80	7 w	75
9	2 S	8	30	10 S	28	80	equals	35
10	2 S	9	35	8 S	30			
12	2 S	10	40	3 S	35			

Since the observation is now made for the first time, that highly concentrated caustic soda has notably less effect in increasing the affinity of cotton yarn for substantive colours than has a solution of less strength, it seemed desirable to repeat some of the trials. Hanks of the same spinning as before were therefore steeped in caustic solutions of concentrations ranging from 50°—80° Tw. for 48 hours, and, after the usual exhaustive washing and drying, were dyed with Benzopurpurin 4 B, using one-eighth per cent. by weight of colour ·

on the weight of the hanks; the application of less dyestuff than in the previous tests seemed desirable in order to facilitate the subsequent comparison of the dyed hanks. The results tabulated below (Table II.) were thus obtained, and confirm the previous conclusion that the most concentrated soda solutions have less effect in increasing the affinity for the benzopurpurin than those of less concentration, although in the second set of trials the turning point seems to be with soda of between 65° and 70° Tw., whilst in the earlier trials the turning point appeared to lie between 70° and 75° Tw. This slight apparent discrepancy might, perhaps, be attributable to the different amounts of colour used in the two sets of tests, or might possibly arise from the difficulty of appreciating such slight variations of shade as are involved; its true reason is, however, almost certainly to be found in the circumstance, which is further discussed below, that a hank treated with a very strong lye, on washing with water, becomes for a certain time impregnated with a rather more dilute and therefore more active lye. In any case the fact is clear that soda of 80° Tw., when applied to cotton yarn, does not increase the affinity for substantive colours to nearly the same extent as does soda of 70° Tw.; further, the concentration of soda which produces the maximum effect in this respect appears to have a density of between 60° and 70° Tw.

TABLE II.—Yarn treated at 20°C. with Soda of various concentrations for two days, and dyed with one-eighth per cent. by Weight of Benzopurpurin 4 B.

Soda of ° Tw.	Relative Strength of Dyeing.	Compared with Soda of Strength in ° Tw.
50	3 s	45
55	2 s	50
60	s	55
65	s	60
70	w	65
75	w	70
80	w	75
80	equals	55

The reversal of the action of the soda in increasing the affinity for colour during continuous increase in the concentration of the soda with which the cotton is treated, is further of interest in that it might be connected with the generally held view that cold caustic has a more powerful mercerising action than soda of the same concentration at a high temperature. Therefore a series of dyeing trials was made, with hanks of the same kind of cotton as in the previous case, using caustic of 10°, 20°, 30°, 40°, and 50° Tw., steeping a hank in each solution at 20°C. and at 80°C. respectively, and keeping the solutions well stirred in the ordinary way to ensure uniform action of the caustic; after washing until free from soda, the hanks were dried and dyed all together in a boiling solution of Benzopurpurin 4 B, using 1 per cent. of colour on the weight of the hanks.

On matching the hanks the results tabulated below (Table III.) were obtained, the same roughly quantitative method of description as was previously used being adopted.

TABLE III.

Soda of °Tw.	—	Soda of °Tw.	Soda of °Tw.	—	Soda of °Tw.
10, hot ...	s ...	Untreated.	40, hot ...	4 s ...	20, cold.
10, cold ...	2 s ...	10, hot.	30, cold ...	5 s ...	40, hot.
20, hot ...	2 s ...	10, cold.	50, hot ...	s ...	30, cold.
30, hot ...	3 s ...	20, hot.	40, cold ...	5 s ...	50, hot.
20, cold ...	2 s ...	30, hot.	50, cold ...	5 s ...	40, cold.

The result of this test is a very remarkable one; it is found that whilst caustic of 20° Tw. applied hot causes ultimately a slightly stronger dyeing than 10° Tw. soda used cold, 30° Tw. soda applied hot gives less depth to the resulting dyeing than does 20° Tw. soda used cold. The difference in action becomes accentuated as the strength of the soda is increased; and so it is found that soda of 50° Tw. applied at 80°C. affects the hank in much the same way—so far as its affinity for colour is concerned—as 30° Tw. soda used cold. It seems to have escaped previous observation that caustic soda in such low concentrations of lye as 1° or 2° Tw. has quite a considerable action in increasing the affinity of the cotton towards substantive dyestuffs; and this is the more remarkable in that it is frequently customary to boil yarn in caustic of 1° or 2° Tw., or even of slightly greater concentration, as a preliminary to bleaching. In order to throw further

TABLE IV.

Strength of Soda. °Tw.	Strength of Dyeing.	Strength of Soda. °Tw.
1, cold	3 s	Untreated.
2, cold	3 s	1, cold.
3, cold	3 s	2, cold.
1, hot	2 w	1, cold.
1, hot	w	Untreated.
2, hot	2 s	1, hot.
2, hot	equals	Untreated.
3, hot	s	2, hot.

light on the question which here arises, a series of trials was made in which the same yarn as before was steeped in caustic soda of 1°, 2°, and 3° Tw., both at 20°C. and at 100°C. for 15 minutes, and, after exhaustively washing the hanks treated cold with cold water and those treated hot with boiling water, all the hanks, together with an untreated one for purposes of comparison, were dyed in the same bath with ¼ per cent. of their weight of Benzopurpurin 4 B. The results obtained on matching these hanks are stated in Table IV. The table makes it clear that the prevalent practice of boiling yarn with a 2° Tw. soda solution has no effect in increasing the affinity of the cotton for substantive colouring matters, although the same concentration of soda applied cold causes a very considerable deepen-

ing of the shade ultimately assumed by the yarn. Many other chemical reagents are known which produce on cotton an effect superficially similar to that obtained with caustic soda, and which also give to the cotton an increased affinity for substantive colours; in order to ascertain whether a different influence is exerted on the dyeing properties by such substances when applied in solutions of different concentrations, several series of trials have been made with a number of reagents, using in each case solutions of various concentrations. Hanks of bleached cotton were steeped during the same time in solutions of different concentrations of the particular reagent, then washed, dried, and dyed in a bath containing 3 per cent. of Benzopurpurin 4 B on the weight of the hanks. The results of matching the hanks are given in the appended table (Table V.) :—

TABLE V.

Barium Mercuric Iodide.

6 vols. sat. sol. to 6 vols. water ·	...	s	...	Untreated yarn.
6 „ „ „ 4 „ „	...	s	...	4 vols. sat. sol. and 6 vols. water.
8 „ „ „ 2 „ „	...	s	...	6 „ „ „ 4 „ „
Saturated solution	...	5 s	...	8 „ „ „ 2 „ „

Potassium Iodide.

°Tw.				°Tw.	°Tw.				°Tw.
2	......	s	......	Untreated	40	......	equals	......	20
				yarn	75	......	s	......	40
5	......	s	......	2	105	......	s	......	65
10	......	s	......	5	Saturated	......	s	......	105
20	......	s	......	10	sol.	......		......	

Hydrochloric Acid.

°Tw.				°Tw.	°Tw.				°Tw.
5	......	s	......	Untreated	25	......	2 s	......	20
				yarn.	30	......	s	......	25
10	......	s	......	5	33	......	s	......	30
15	......	s	......	10					
20	......	equals	......	15					

Zinc Chloride.

2 per cent. solution	......	s	......	Untreated yarn.
4 „ „	......	s	......	2 per cent. solution.
10 „ „	......	equals	......	4 „ „
30 „ „	......	2 s	......	10 „ „
50 „ „	......	2 s	......	30 „ „
70 „ „	......	5 s	......	50 „ „

Nitric Acid.

°Tw.				°Tw.	°Tw.				°Tw.
5	......	s	......	Untreated	65	......	2 s	......	50
				yarn.	83	......	10 s (and	......	65
10	......	s	......	5		......	yellower).	......	
20	......	2 s	......	10	100	......	5 s (and	......	83
35	......	2 s	......	20		......	yellower).	......	
50	......	2 s	......	35					

The consideration of the above sets of dyeing trials shows that each of the reagents dealt with behaves somewhat similarly to caustic soda, so far as concerns the increase in the affinity for colour which it gives to the fibre. That is to say, as the concentration of the solution increases, the affinity of the cotton for the substantive colour also increases; in no case, however, have we been able to observe the reversing effect which is produced with soda. The work described above having established beyond doubt that caustic of high concentration has a less effect in increasing the affinity of cotton towards substantive colours than has soda of somewhat lower concentration, it seemed desirable to ascertain whether other properties of cotton are similarly related towards the strength of soda with which yarn has been treated; that is to say, whether any other property can be discovered which increases in magnitude as the concentration of the soda increases up to a certain limit, beyond which its magnitude decreases with a further increase in the strength of the soda solution applied. A great number of attempts were made to determine accurately the shrinkage which the application of soda solution causes in cotton yarn, but for a long time these attempts proved abortive. The extent of the shrinkage is so slight, especially with dilute soda solutions, that the small but unavoidable amount of stretching to which the yarn is subjected during the final washing makes the results appear very confusing. Ultimately, we found it possible to take measured lengths of yarn, steep them in caustic soda for a given time, and then to measure their lengths again by re-reeling whilst the yarn is still soaked with lye; both the reelings are effected on a small machine in which the yarn passes between two wheels, the lower, of about six inches diameter, being connected with a counting mechanism, and the upper one being merely a small but heavy cylinder, the object of which is to keep the yarn uniformly stretched during its passage between the two wheels. Hanks of 200 yards each of a bleached tightly twisted yarn were steeped in caustic soda of various concentrations during half an hour, and then re-reeled in the manner briefly described; three parallel sets of determinations were made, and the mean of each set of three corresponding observations is given in the accompanying table (Table VI.). In order to facilitate the comparison of these observations on the extent to which cotton yarn is shrunk by treatment with caustic soda with the results obtained in the previous dyeing trials of similarly treated yarn, it is convenient to plot the shrinkage against the strength of the soda. For this purpose the curves expressing the relation between the strength of the dyeing and the strength of the soda and between the amount of shrinkage and the strength of the soda are shown in the same figure (Fig. 1). An inspection of the table shows that the most dilute caustic soda, even of 1° Tw., exerts an
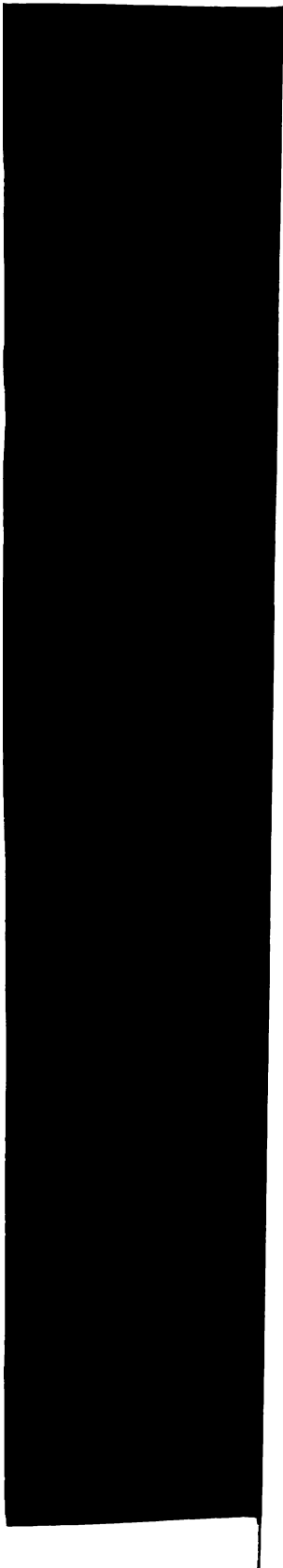
appreciably greater shrinking action on the yarn than does pure water in the cold. As the concentration of the soda is increased, however, the shrinking effect is seen to increase fairly uniformly up to about 18° or 20° Tw. concentration, whilst at about 20° Tw. a sudden increase in the amount of shrinkage effected is observed to occur. As is pointed out below, this concentration of soda is about

TABLE VI.

Strength of Soda.	Length of Hank after treatment.	Strength of Soda.	Length of Hank after treatment.
°Tw.	Yards.	°Tw.	Yards.
0	198·0	22	171·3
1	196·4	24	163·1
2	195·7	26	160·3
3	195·6	28	160·0
4	195·5	30	158·2
5	195·2	35	150·2
6	194·2	40	143·7
7	193·7	45	141·0
8	194·2	50	142·2
9	194·0	55	142·7
10	194·2	60	145·3
12	194·5	65	149·2
14	192·7	70	150·3
16	190·4	75	152·8
18	188·7	80	154·2
20	186·8		

the same as that which shows the first appreciable action on the microscope stage upon the cotton fibre. Above 20° Tw. the extent of the shrinkage increases with the concentration at a far more rapid rate than before, and the greatest shrinking effect is obtained with soda of 45° Tw.; as the strength of the soda is increased above this concentration, the shrinkage observed diminishes continuously until the concentration of 80° Tw., the highest which we have applied, is reached. The results now put forward find an important practical application in the action of soda of different concentrations on a technical scale. It is seen from Table VI. that the maximum shrinkage is obtained when yarn is treated with soda of about 45° Tw., but it was observed that on treating yarn with soda of 80° Tw. and obtaining the slight amount of shrinkage which is noted in the table, a further and quite considerable shrinkage took place during the subsequent washing. This is of course only what would be expected, inasmuch as the yarn impregnated with soda of 80° Tw.—a liquid of high viscosity—when treated with water becomes impregnated with soda of greater dilution, and the degree of dilution increases as the washing proceeds. Consequently the initial shrinking effect of 80° Tw. soda on the yarn is that noted in the table, but the action which is exerted during the washing with water is, at any rate during the early stages of the washing, the

action of a soda which has a much greater shrinking effect on the yarn, such for instance as soda of 50° Tw. On impregnating yarn with soda of about 50° Tw., and afterwards washing with water, no perceptible shrinking is observed during the washing, the reason being that the dilution has the effect of making the soda less active than before towards the yarn, so far as shrinking action is concerned. If we, therefore, consider what will happen during the impregnation of yarn on the mercerising machine or of a cotton fabric during treatment on the stenter, it will be seen that with soda up to, say, 50° Tw. the main shrinkage will occur during impregnation with soda, whilst during the subsequent washing no additional strain will be put on the arms of the yarn mercerising machine or on the clips of the stenter. The conditions are, however, quite different when the yarn or fabric is impregnated with soda of a higher degree of concentration, say, of 75° or 80° Tw. In this case less shrinkage takes place during the actual impregnation, but, on washing afterwards with water, the yarn or fabric tends to undergo a further and considerable contraction; with the high concentration of soda, therefore, the greatest strain is exerted on the arms of the mercerising frame or on the clips of the stenter during the early stages of the washing with water. There is thus in this case a certain tendency for the yarn to tear or for the cloth to rip, which would be avoided if a more dilute soda had been employed. In connection with the dyeing properties, it is further clear that the application of soda of 70° or 80° Tw. will have a tendency to make the yarn or fabric dye unevenly because of the more powerful action on the affinity for dyestuffs exerted by the lower concentrations of soda, which will be produced locally during washing. On inspecting the curves given in Fig. 1 it will be seen that whilst the greatest increase in the affinity of cotton for substantive colours is contributed by the action of soda of about 70° Tw. concentration, the greatest shrinkage is observed when soda of a much lower concentration is applied, viz., of 45° Tw. This is doubtless due to the operation of the cause referred to in the preceding paragraphs, viz., to the fact that the treatment with soda of 80° Tw. and afterwards washing involves the action, at any rate for a short time, of soda of all lower concentrations on the fibre; this would lead to the yarn treated with soda of 80° Tw. and subsequently washed, dyeing much more strongly than would have been the case if, after immersion in the 80° Tw. soda, the whole of the soda could have been removed from the yarn without adding water. It should, however, be noted that on washing a yarn shrunk by the impregnation with caustic soda, some change in the length of the hank must be expected to occur quite independently of any alterations in length produced by the action of diluted soda temporarily formed; the extent of such action is still under investigation.

So far as the present trials can be interpreted, it would seem that a great deal of evidence exists indicating that the apparently increased affinity which cotton has for colouring matters after having been treated with soda is, in the main, proportional to the extent to which shrinkage has taken place. We have now in hand a series of tests intended to elucidate this matter still further; tests in which the yarn, after immersion in strong soda, is washed free from soda with alcoholic solvents under such conditions that the action of aqueous caustic soda solutions of lower concentrations can play no part. A highly special case of such proportionality between the shrinkage and the strength of the dyeing would be that in which a given length of yarn removes the same weight of dyestuff from the bath when it is mercerised as when it is unmercerised; the greater depth of colour exhibited by the mercerised hank would here be due solely to the same weight of colour being distributed throughout a shorter length of yarn than would be the case with the unmercerised hank. We find, however, on taking two hanks of the same length and dyeing them both in separate baths of the same concentration, the one after and the other before mercerisation, that the exhaust from the mercerised hank is much paler in colour than that from the unmercerised hank. The proportionality is consequently not of the special and simple character last mentioned above. We now turn to the microscopic examination of the changes produced in cotton by treatment with mercerising and other liquids. The microscopic examination of cotton offers certain difficulties which arise principally from the high degree of transparency possessed by the fibre; these difficulties are greater after the cotton has been treated with mercerising agents because the apparent transparency of the fibre as it lies on the microscope stage is much greater than before the treatment. Further, if mounting agents are used in the preparation, more difficulty is experienced in the microscopic observation owing to the refractive index of the fibre approximating to that of the medium, and to the consequent loss of definition. It therefore seemed desirable to apply some artificial method of increasing the microscopic definition, and resort was made to the examination of the fibres between crossed Nicol prisms, a polariser being inserted under the sub-stage condenser and an analyser being placed in the eye-piece in such a position that its principal section lay at right angles to that of the polariser. The statement has been made (compare Guttmann, *Manufacture of Explosives*, 1895, vol. 2, p. 59) that under these conditions ordinary cotton appears colourless, but actual experience shows that all cotton fibres show interference colours when examined microscopically between crossed Nicol prisms. The interference colours exhibited by raw cotton when examined in this way are not very brilliant; they are doubtless due to internal strain in the otherwise amorphous material of which the fibre is composed and, the

strain being apparently but slight, the colours are of such a, high interference order that they are not visually brilliant. In order to enhance the brilliancy of the interference colours the authors prefer to insert above the polariser, and with its principal direction at $45°$ to that of the polarising and analysing prisms, a mica plate of such thickness as to increase the retardation of the light passing through the preparation by one-eighth of a wave-length; this thickness of mica plate seems ordinarily to give the best results, but the most appropriate thickness for use in any particular case so as to obtain the maximum colour effect in the fibre is readily ascertained by passing a quartz wedge of the ordinary kind between the eye-piece and the preparation, and noting when the most brilliant display of colour is made by the fibres. The microscopic examination of the cotton fibre between crossed Nicol prisms, with the interposition of a one-eighth wave-length retardation plate in the manner just described, not only facilitates the observation of the outline of the fibre, but enables the internal canal, cracks in the fibre, and internal peculiarities of all kinds to be made out with great ease, the differences in thickness of various parts of the fibre being indicated by changes in the colour exhibited. The photographs in natural colours which illustrate this paper have been made by the Sanger-Shepherd process in elliptically polarised light under the conditions of illumination described above.

The microscopic examination of the raw cotton fibre shows it to consist of a flattened ribbon, the edges of which are somewhat thickened and usually slightly turned up; sometimes, however, the edges are turned up to such an extent that they stand at nearly right angles to the surface of the ribbon. The best drawings of the cotton fibre which have previously been published are undoubtedly those given by Walter Crum (J. Chem. Soc., 1863, p. 404). These pictures give a good idea of the general microscopic appearance of raw cotton and show the slight thickening of the edges referred to; in polarised light, however, the internal canal is distinctly visible as a flattened tube-like structure traversing the whole length of the fibre. Crum's drawings are, however, faulty in one respect, namely, that the natural twist in the fibre is not of the loose character which he depicts, but is flattened, so that the twisted fibre has rather the appearance of a ribbon which has been twisted and creased rather than that of one which has been merely twisted. It is sometimes stated that the natural twist of the cotton fibre always runs in the same direction. That this is not so is sufficiently indicated by Crum's drawings, and is also evident on the most superficial microscopic examination of the fibre; the fibre is sometimes twisted in the one direction and sometimes in the other. Further, the same fibre is generally twisted in parts to the right and in parts to the left, several

changes in the direction of twist being noticeable throughout the length of a single fibre; this change in twist is of great importance in connection with the production of lustre during mercerisation, as will be pointed out below. Fig. 2 represents the photograph of a plain or untreated cotton fibre taken in polarised light as above described, and in Fig. 3 is reproduced the same fibre photographed in natural colours. On placing a few fibres of loose cotton on a slide under a cover glass on the microscope stage, and carefully watching the behaviour of the fibres as a drop of caustic soda placed on the slide gradually comes into contact with the fibres, no change at all is observable in the cotton until the strength of the soda used reaches 16° Tw. At this concentration, however, it is seen that the fibres untwist slightly during the two or three seconds after the soda has come into contact with them; the untwisting is very incomplete and is at an end within three seconds or so at the ordinary temperature. On increasing the strength of the soda gradually, the same kind of behaviour is observed until a concentration of 20° Tw. is reached, and here the initial untwisting, which still proceeds with great rapidity, is followed by a very slow uncoiling of the twist of the fibre; but even at this strength of soda the fibre never becomes quite unrolled. With soda of 22° Tw. bubbles of air begin to make their appearance in the internal canal, and the transparency which the liquid gives to the fibre is produced much more slowly than with lower concentrations of soda. At a concentration of 26° Tw., the initial rapid and the later slower untwisting action become confused and only one kind of uncoiling effect is distinguishable; that is to say, the fibre uncoils slowly and regularly during a period of about five seconds and the fibre is left as a somewhat flattened ribbon, which is still slightly twisted. At 28° Tw. the action of the soda is appreciably slower; the uncoiling proceeds for about 15 seconds and has the effect of removing practically all the twist from the fibres; at the same time, the becoming transparent, which apparently indicates the soaking in of the soda, proceeds much more gradually than before, and the running of the soda through the internal canal with the formation of air-bubbles is much more distinctly visible than at the lower concentrations. With soda of 30° Tw. the twist of the fibre for the first time disappears completely. With soda of 35° Tw. the untwisting still proceeds with fair rapidity, occupying about 15 seconds for completion, and after the untwisting has become practically complete the fibre is seen to swell, the swelling being accompanied by an increase in the transparency of the fibre; the two changes are, however, quite distinct, the swelling following the untwisting. At 40° Tw. fewer air-bubbles are produced than before and the swelling proceeds more rapidly, so that one part of the fibre is seen to be swelling whilst another part is still in the stage when untwisting is

taking place. At 45° Tw. no air-bubbles are left in the canal, and the latter almost completely disappears; the swelling and untwisting go on quite simultaneously, and the whole action is complete in about 15 seconds.

The behaviour of the fibres towards soda of 50°Tw. is similar to that towards the 55° Tw. solution, with the exception that the action is a trifle less rapid with the lye of higher concentration. With soda of 55° Tw. it is for the first time noticed that a perceptible interval elapses between the wetting of the fibre and the commencement of the uncoiling; this interval occupies about three seconds, and the subsequent action is completed in about 20 seconds. With lye of 60° Tw. no appreciable change occurs for the first eight seconds or so, and then the fibres begin to swell and to become transparent; after the swelling has occurred the fibres begin to untwist, and the uncoiling takes place very slowly and deliberately, requiring about a minute for completion. With soda of 65° or 70° Tw. the same kind

TABLE VII.

Strength of Soda in °Tw.		
0 to 15	...	No apparent effect.
16 to 18	...	Incomplete uncoiling during about a second.
20	...	Initial rapid untwisting followed by sluggish ditto.
26	...	Rapid and slow uncoiling become one, lasting 5 seconds.
35	...	Untwisting followed by swelling.
40	...	Untwisting and swelling proceeding together.
60 to 80	...	Swelling precedes untwisting.

of action proceeds, the swelling preceding the uncoiling and the whole action going still more slowly, so that with 70° Tw. soda, evidence of action is still visible after two minutes' contact. Soda of 75° Tw. exerts no apparent action for at least a minute and takes about four minutes for completion; the air-bubbles assume irregular shapes in the internal canal, giving an impression as if the fibre had burst open. With soda of 80° Tw. concentration the action takes a still longer time, and nearly all the fibres appear as if burst or split; a photograph of one of these burst and swollen fibres is reproduced in Fig. 4. In order to facilitate their comparison these observations may be conveniently epitomised in a table (Table VII.). The untwisting of the cotton fibre under the influence of caustic soda has not been referred to by previous workers in this field; it has the effect, when the cotton is mercerised loose, of converting the fibre into a plain surfaced rod which is bent more or less irregularly, and which is very much matted together or entangled with other fibres. The entanglement of the fibres caused by the writhing which attends the immersion in strong soda is of course responsible for the difficulties which have made the spinning of cotton which has been mercerised loose a practical impossibility. As a point of great importance, which we now call attention to for the first time, is to be noted that

up to a concentration of about 40° Tw. the swelling action of the soda follows the untwisting, whilst at concentrations greater than 40° Tw. the reverse is the case, the untwisting following the swelling. Since the concentration of about 40° Tw. is the lowest at which an effective mercerising action for practical purposes can be effected, it follows that the production of a lustre on cotton is necessarily connected with the action of soda of such concentration as causes the untwisting of the fibre to take place, either after the swelling is at an end or simultaneously with the occurrence of the swelling. The new observation, namely, that strong caustic causes the cotton fibre to untwist, is therefore one of the determining factors in the production of a gloss during the mercerising of cotton. Confirmation of this view, if it be correct, should be obtainable by investigating microscopically the action of hot caustic soda solutions on the fibre, because it is known that hot soda is not nearly so effective a mercerising agent as is the same concentration of soda in the cold. A caustic soda solution of 50° Tw. was taken, which at 20°C. produces a brilliant lustre on stretched Egyptian yarn and at 90° gives a lustre which is much less marked; on steeping the fibres in this at 20°C. on the microscope stage, the appearances noted in Table VII. were observed, namely, that the fibres swell slowly and afterwards untwist; but on arranging the microscope stage so that the fibres can be examined under the influence of the soda solution at 90°C., it is seen that at the high temperature the fibres began to untwist rapidly immediately they come in contact with the hot soda, and that after this untwisting is at an end the swelling effect sets in, but not until the whole of the uncoiling is finished. It is, therefore, clear that the necessary condition for the production of a good lustre during mercerisation is that the untwisting should follow the swelling, or at least that both swelling and untwisting should proceed simultaneously; and that the inefficiency of hot as opposed to cold caustic soda in mercerising is due to the fact that with the cold caustic the swelling precedes the uncoiling, whilst with the hot caustic the untwisting takes place first. The production of a lustre during the mercerisation of stretched yarn has been previously attributed wholly to the shrinkage and the swelling which takes place during the action of strong caustic soda. It has now been shown that a new factor, namely, the untwisting of the fibres, is also a necessary one to the production of an appreciable gloss. The importance of this conclusion is such as to make further confirmatory evidence desirable before proceeding to discuss the exact way in which the untwisting is operative in giving rise to the lustre. An examination was therefore made of the action of a number of other reagents on the cotton fibre, using the same kind of method of microscopic examination as in the above experiments. The results are here given.

Action of a Mixture of ten parts of Soda Lye of 28° B and one part of Water-glass Solution of 41° B. The use of a mixed solution of water glass and caustic soda of the above composition has been patented by Meister, Lucius and Brüning (Eng. Pats. 10,784 of 1897 and 11,313 of 1897), and, as Gardner remarks (*Mercerisation der Baumwolle*, 1898, 44), the lustre produced by it is inferior to that obtained with caustic soda alone; the mixture hinders the shrinkage, although it increases the affinity of the yarn for colouring matters. On allowing the mixture to act upon cotton fibres on the microscope stage, it is seen that action sets in slowly, the fibres beginning to untwist rapidly after about five seconds' contact with the solution and becoming quite straight after about 20 seconds. At the same time swelling occurs, but to a far less extent than if caustic soda solution alone is used. Measurements made on a hank steeped at 20°C. and subsequently washed and dried showed that shrinkage to the extent of 17·4 per cent. was caused by the action. The hank treated with this solution in the unstretched condition showed slightly more gloss than the raw yarn, whilst a hank immersed and washed whilst stretched exhibited a distinct lustre, although far less than if strong caustic alone had been used in the treatment. Treatment with this solution thus causes untwisting and but comparatively slight swelling and shrinking; and the faulty nature of the lustre produced is traceable to the incomplete extent to which these two latter factors participate in the action.

Action of a Mixture of two parts of Soda Lye of 38° B with one part of Glycerin. The use of this mixture for mercerising purposes has been protected by the Farbenfabriken vorm. F. Bayer and Company (D.A.Kl. 8, 10,126 of 1897), and is said to arrest the shrinkage whilst increasing the strength of the yarn. It was found on immersing a hank of bleached Egyptian yarn in the mixture, and afterwards washing and drying, that a shrinkage of 13·4 per cent. took place. The yarn immersed unstretched showed a slight gloss, and a hank immersed in the stretched condition developed more lustre, although far less than if caustic soda alone had been used. Treatment of loose cotton on the microscope stage with the solution showed that the fibres at first swell very gradually, with the accompaniment of but little untwisting; after two minutes' action the fibres are still seen to be swelling slowly, but the untwisting begins to proceed more rapidly. The whole action is far less marked than if ordinary soda lye is used, but after the expiration of about four minutes the fibres are seen to have assumed somewhat the appearance of cotton fibres which have been mercerised in the stretched condition. This seems to be due to the slow swelling having partly absorbed the twist in the fibre, and in such a way that traces of it still remain as ridges on the round swelled surface of the fibre.

Action of Sulphuric Acid. Mercer found that sulphuric acid exerts an action upon cotton superficially resembling that of soda. The authors found that on steeping a hank of bleached Egyptian yarn in sulphuric acid of 114° Tw., and subsequently washing and drying, a shrinkage to the extent of 9·5 per cent. in length is obtained; at this concentration, however, the fibres are rapidly attacked and partly dissolved. A hank immersed stretched shows after washing a perceptible increase in lustre. The examination of the action on the microscope stage shows that the fibres rapidly untwist immediately they come in contact with the acid and at the same time swell and shorten. More rapid untwisting and dissolution is observed with concentrated sulphuric acid.

Action of Zinc Chloride Solution. This reagent was also mentioned by Mercer as somewhat similar in its action to caustic soda. The microscopic examination of the action of a 50 per cent. solution shows that the fibres untwist very slightly at the moment of contact with the solution, but that the uncoiling stops and does not again set in; slow swelling and shrinking are noticeable. A hank immersed loose was found, after washing and drying, to have shrunk by 2·3 per cent. and showed no lustre; a stretched hank, however, was found to have become very slightly lustrous.

Action of Syrupy Phosphoric Acid. The shrinking action of strong phosphoric acid solution was also mentioned by Mercer. The authors find that no action is observable for the first minute and a half after phosphoric acid is brought into contact with the fibres on the microscope stage; the fibres then, however, begin very slowly to untwist and afterwards to swell. This action proceeds until the material goes into solution.

Action of Nitric Acid of 83° *Tw.* Fibres treated on the microscope stage with strong nitric acid unwind very rapidly; they swell, however, only very slowly and to a considerably less extent than with caustic soda. The shrinkage of yarn immersed loose in nitric acid of 83° Tw. amounts to 9·5 per cent. Yarn treated under tension exhibits a distinct lustre, which is, however, inferior to that produced by strong caustic, and is about the same as that obtained with the mixture of caustic soda and glycerin.

Action of Concentrated Hydrochloric Acid. On immersion in the liquid the fibres are seen to untwist rapidly, although not so rapidly as in strong caustic soda; slight swelling and shrinkage also occur. A hank immersed loose was found to have shrunk by only 1·8 per cent. after washing and drying, but exhibited no lustre, whilst a hank immersed stretched developed a distinct lustre.

Action of Sodium Sulphide Solution. The application of a 30 per cent. sodium sulphide solution for producing a silky lustre on stretched yarn was protected by Schneider (P.B.A., Kl. 8, 12,196 of 1896). It was found that immersion in such a solution caused a shrinkage of 1·3 per cent. in the length of the hank. The yarn, immersed either stretched or unstretched, acquires lustre during the treatment, although not to anything like the same extent as when caustic soda is applied to stretched yarn. On the microscope stage the fibres are seen to untwist and to swell but slightly.

Saturated Potassium Iodide and Potassium Mercuric Iodide Solutions. It has previously been shown that saturated potassium iodide and potassium mercuric iodide solutions have a considerable action on cotton yarn. On immersing a hank in saturated potassium iodide solution it shrank by 2·3 per cent. in length, and a hank immersed stretched acquired merely a slightly increased lustre. The same slight increase in lustre was obtained on immersing a stretched hank in saturated potassium mercuric iodide. On the microscope stage no untwisting of the fibre can be observed, and only a slight swelling occurs either with potassium iodide or with potassium mercuric iodide.

Saturated Barium Mercuric Iodide Solution. The authors have shown that saturated barium mercuric iodide solution causes shrinkage and an increase in strength in cotton yarn practically equal to that produced by caustic soda of 65° Tw. (*Journal of the Soc. of Chem. Ind.*, 1903, 70-77). On microscopic examination saturated barium mercuric iodide solution is seen to cause no untwisting at all in the fibres, although great swelling and shrinkage occur. A hank immersed stretched developed but a slight lustre. No action could be detected on treating the fibres with *formic* or *glacial acetic acid*, or with *ammonia* on the microscope stage. On inspecting the results given above it will be seen that the liquids which cause rapid untwisting, strong swelling, and considerable shrinkage, namely, caustic soda, soda with water glass, soda with glycerin, and nitric acid, are those which cause the stretched yarn to acquire considerable lustre. These three factors, in the authors' view, are essential to the production of any considerable lustre, and it will be noted that when only two of these factors are operative no appreciable lustre is developed on the stretched yarn. Thus, sodium sulphide and hydrochloric acid cause rapid untwisting of the fibre, but only give rise to slight swelling and shrinking; treatment with these liquids leads to the production of but little lustre on the stretched yarn. Again, barium mercuric iodide solution causes great swelling and shrinking, but does not make the fibre untwist; this liquid, consequently, gives rise to the production of but little lustre on the stretched yarn. Lastly,

zinc chloride, potassium iodide, and potassium mercuric iodide cause no untwisting and but slight swelling and shrinkage; their application is thus attended by the production of but very little lustre in the stretched hank.

A final, but probably the most convincing of all the confirmations of the truth of the view that untwisting, swelling, and shrinkage must co-operate for the production of a lustre in the treatment of cotton is to be found in some results which the authors have previously published (*Journal of Soc. of Chem. Ind.*, 1903, 70-77). A hank, 66 cm. in length, of an unbleached Egyptian yarn, having the breaking load of $417\cdot4 \pm 2\cdot1$ grms., was immersed in caustic soda of 65° Tw., and, after washing and drying, was found to have shrunk in length to $44\cdot8$ cm. and to have increased in strength to $526\cdot3 \pm 3\cdot8$ grms. A similar hank immersed in saturated barium mercuric iodide solution, after washing and drying, had shrunk to $48\cdot9$ cm. in length, and its breaking load had increased to $526\cdot6 \pm 3\cdot3$ grms. The shrinkage and increase in strength effected by these two solutions was, therefore, nearly the same as could be produced during any test of a practical nature, and consequently the authors can state that the swelling and the shrinkage caused were identical in the two cases. The only other difference is that in the case of the caustic soda rapid untwisting of the fibre takes place, whilst with the barium mercuric iodide no such uncoiling of the fibre can be observed; consequently, a stretched hank treated with this soda solution developed a perfect lustre, whilst a stretched hank immersed in the barium mercuric iodide solution showed scarcely any increase in lustre. The proof that the production of a lustre on treating cotton yarn with reagents whilst in the stretched condition is dependent to as great an extent upon the newly observed property of untwisting which the fibre possesses as upon the previously observed factors of swelling and shrinking is completed by the above observations. Attention may now be given to the consideration of the purely mechanical effect which causes yarn mercerised under tension to appear lustrous. It has been remarked above that after mercerising and washing loose cotton fibres they appear as plain smooth surface rods; the internal canal is almost obliterated and the fibre is curved or bent more or less abruptly. The authors have, however, not been able to confirm the observation of Lange (Färberzeitung, 1898, 197) that the surface of the fibre mercerised loose exhibits many folds; the fibres after treatment show extremely regular surfaces and very few folds or creases are observable at all. Further, the absence of the folds to which Lange refers is plain from the photographs which he himself gives in illustration of his paper. The photograph, taken in polarised light in natural colours, which is now given (Fig. 5) of the appearance of a quite typical cotton fibre which has been mercerised loose, renders

quite clear the strong contrast between the appearance of a raw cotton fibre (Fig. 2), also in polarised light, and the fibre mercerised loose. On stretching a raw cotton fibre on the microscope slide, fixing it at its two ends in a stretched condition by means of drops of wax applied at the two ends, and then watching it on the microscope stage whilst caustic soda of 65° Tw. is acting upon it, a clue is got to the true reason of the gloss produced during mercerisation. The fibre is seen to first straighten itself and then to swell under the action of the reagent, the twist remaining for the most part. After the fibre has become rounded, gelatinous and swollen by the absorption of the soda, the untwisting begins to set in. It will be remembered that (as shown above) with solutions sufficiently concentrated to effect mercerisation, the fibres first swell and afterwards or simultaneously untwist. One part of the fibre held at the two ends is seen to become twisted owing to the untwisting of some other portion of the stretched fibre; later, another part is seen to twist, perhaps in the reverse direction to the first, owing to some other part of the fibre giving up its natural twist. This kind of action goes on until the original and natural twist of the fibre has become more or less replaced by the second kind of twist produced by the previous unwinding. The fibre mercerised stretched thus presents the appearance of a gelatinous straight rod on which a series of pieces of corkscrew-like windings are visible; on washing the fibre and allowing it to dry, it is seen to preserve this shape. By this process the original creased or folded ribbon which constitutes the raw cotton fibre becomes converted into a straight rod of nearly circular cross section which carries on its surface, however, a series of spiral elevations; at the same time the fibre and the surfaces of the raised ridges are perfectly smooth; the rounded surfaces of these smooth ridges reflect the light which falls on them from any direction in just the same way as do the turns in a polished corkscrew, and it is to the presence of these ridges, which are absent in the original fibre or in the fibre mercerised loose, that the increased lustre of cotton yarn mercerised in the stretched condition is due. For the purpose of illustrating the appearance of these ridges on a cotton fibre mercerised in the stretched condition the photograph in natural colours of a typical fibre is given in Fig. 6; for purposes of comparison a photograph of a similar fibre taken in polarised white light is shown in Fig. 7.

Lange (*loc. cit.*) has ascribed the lustrous appearance of cotton mercerised stretched to the fibre having been subjected to tension whilst still elastic, and states that such fibres present the appearance of "rods which are fairly straight, stretched, and transparent, with—in comparison with the fibres which have been mercerised in the loose state—smooth, regular surfaces." The fibres, he remarks,

have the appearance of "a smooth tube." That the authors' view is correct and that Lange's is not, can be easily seen on examining a mass of fibres which have been mercerised stretched, either as such or in yarn, upon the stage of a dissecting microscope under a magnification of 20 to 40 diameters, allowing the light from some powerful illuminator to fall directly upon the fibres. It will be seen that the lustre or sheen of the whole mass of fibres is not due to a reflection of light from the whole or a considerable part of the length of the individual fibres, but is due to reflection from a number of points on each fibre, that is to reflection from the sides of the ridges lying spirally on the surface of the fibre. Again, the cross section of a cotton fibre mercerised loose is nearly circular, and, if Lange is correct in his view that the stretching during mercerisation has the effect of rendering the fibre smoother and more tube-like in appearance, the cross section of the fibres mercerised under tension should be still more nearly circular; whilst if the new view which we now advance is correct, the fibre mercerised stretched should be less nearly circular in cross section than the one mercerised loose. This must be so, because amongst a number of sections many would naturally occur in which the section is cut across the ridges; in these cases the cross sections should appear roughly polygonal in outline.

Lange's photographs, which cannot be subject to any bias in the authors' favour, as they were made without any knowledge of the existence of the ridges to which they refer, show very plainly the existence of these polygonal cross sections. It is convenient to construct a rough concrete model to illustrate the efficiency of such a method of obtaining lustre on a smooth polished rod as that of raising ridges on its surface. Fig. 8 represents a photograph of a frame, the upper part of which is filled with smooth-surfaced slightly tapering glass rods, whilst the lower part is filled with similar rods on the surface of which spiral ridges have been made by turning them before the blowpipe. It will be clear from the figure that the smooth rods—which are comparable to cotton fibres mercerised loose—are far less lustrous than the ones carrying the spirals, and which are comparable with cotton fibres mercerised in the stretched condition. It is thus proved that the lustre exhibited by cotton fibres mercerised whilst stretched has a cause which has not hitherto been suspected. The efficiency of the practice sometimes adopted of producing a lustre on cotton yarn or fabrics by immersing them loose in caustic soda and subsequently applying tension, is at once explicable on the basis of our results. The fibres being held in the yarn or fabric cannot untwist entirely and freely as they do when immersed loose in the caustic, each fibre being held by its contact with others in the yarn; when the yarn or fabric is afterwards

stretched whilst still gelatinous from the action of the soda, the fibres are straightened and the smooth and rounded ridges which give rise to the lustre are thereby produced.

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A RECORD OF INVESTIGATIONS
UNDERTAKEN BY MEMBERS
OF THE TEACHING STAFF OF
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OF THE SCHOOL

MCMVIII.

CONTENTS.

RAPID-CUTTING STEEL.

By Prof. J. T. NICOLSON, D.Sc., M. Inst. C.E.

TWO varieties of tool steel have for long been known, and distinguished from each other by the methods employed in hardening them. These are ordinary water-hardened or carbon steel, and self- or air-hardening steel. The latter was discovered by R. Mushet, who found that by the addition of manganese and tungsten to tool steel it maintained its cutting edge at much higher temperatures of the tool point, and that it was consequently possible to cut at much higher speeds than had previously been obtained with water-hardened steel.

THE AMERICAN EXPERIMENTS.

About three years ago an extensive series of experiments was undertaken by Messrs. Taylor and White, at the Bethlehem Steel Company's Works, Pa., U.S.A., upon this question. Their object was to clear up certain obscurities in regard to the hardening of steels, and to find out which brand was most suitable for heavy cutting at high speeds. These experiments appear to have been carried out in a thoroughly scientific manner, and consisted essentially in a long series of tests made upon tools of various chemical compositions, heated to different temperatures. Two hundred tons of forgings were cut up in carrying out the work. The discovery, which was the direct result of these experiments, and which has had such a profound influence on the manufacture of tool steel and upon the design of machine tools, may, perhaps, best be explained by reference to the annexed table of figures, deduced from a curve published in the *Journal of the Franklin Institute* (September 1901). The first line gives the temperatures to which steel of the air hardening variety is heated in the process of hardening, whilst the second line shows the resulting efficiency of the tool steel as expressed by its cutting speed. It will be at once observed that the cutting power falls off very much if the steel is heated above 1550° Fahrenheit, and in the old days steel users were invariably

Temperature (Fahr.) ...	1450°	1500°	1550°	1600°	1650°
Cutting speed (f.p.m.) ...	30	40	43	35	14

Temperature (Fahr.) ...	1700°	1750°	1800°	1850°	1900°
Cutting speed (f.p.m.) ...	16	75	93	108	120

warned by the manufacturers that the tool was not to be heated above a cherry red, otherwise it would be burnt and ruined. But by passing on beyond this "breaking-down point," as they called it,

Messrs. Taylor and White found that, with certain compositions of steel, its efficiency as regards cutting began again to increase, and indeed reached a point far above anything that had before been attained. Even when heated up to 2000° Fahrenheit, at which temperature it softens and crumbles when touched with a rod, the steel, when properly treated in cooling, will cut two or three times as fast as the old Mushet steel could. As a result, the Bethlehem Steel Company were able to astonish visitors by their feats of high-temperature or high-speed cutting at the Paris Exhibition, but as they only performed upon very soft material, much doubt was felt as to the general usefulness of the results of their discovery.

THE GERMAN EXPERIMENTS.

Many practical tests were immediately set on foot in workshops all over the world, but the opinions formed as the result of such sporadic trials were so conflicting that the Berlin Section of the "Verein Deutscher Ingenieure" decided to take the matter up, and in the spring of 1901 they set to work to ascertain the value and applicability of the new steel to general work. The valuable results of the extensive series of experiments which they made were published in the *Zeitschrift des Vereins* for September 27, 1901. For the present article a diagram, Plate I., has been prepared in which a number of these results are reproduced for the benefit of non-German readers. This plate is described below. The Committee of the Verein formed for the purpose of conducting these trials was assisted by the managers of some of the larger engineering establishments, and trials were first undertaken in these. Although seven of the largest workshops in Berlin were available for the experiments, it was found that steels could not be tested therein to the limit of their power on account of : (1) shortage of material under normal working conditions; (2) lack of sufficient power; or (3) insufficient speed upon the lathes. Thereupon the Niles Machine Tool Company placed a large lathe, and the German General Electric Company a motor, at the disposal of the Committee. With this combination a large number of trials was carried out in the Niles Works. The object of the trials was to determine, keeping in view the durability or life of the tools :—

1 What maximum surface could be machined in unit of time with a given cut of $\frac{8}{16}$ inch, the traverse and speed being left open.

2. What weight of cuttings could be removed per unit of time with the greatest possible depth of cut, the traverse and speed being again left open.

The materials operated upon were grey cast iron, cast steel, and forged or rolled Siemens-Martin steel of various ultimate tenacities. The duration of each trial was intended to be two hours. The tool

steels used in the trials were supplied by three firms, namely :—

(a) *Bergische Stahl-Industrie*, of Remschied, who supplied their ordinary air-hardened steel, marked "L."

(b) *Gebrüder Böhler & Co.*, Vienna and Berlin, who supplied two varieties, "Titan-Boreas" and "Rapid."

(c) *Poldi-Hütte*, of Vienna and Berlin, who supplied their steels called "Diamant-ooo" and "Schnelldreher."

BERLIN EXPERIMENTS.—TABLE I.
SIEMENS-MARTIN STEEL.

Brand of steel used.	Trial.	Duration.	Cut.	Traverse.	Area of cut.	Cutting speed.	Weight removed per min.	Surface machined per min.	Skin or not.	Quality of Steel.
	No.	Minutes.	Inches.	Inches.	Sq. ins.	Ft. per min	lbs.	Sq. feet.		
P. S.	261	20	·091	·0670	·0061	194	3·33	0·950	No	..
P. S.	263	63†	·170	·0670	·0114	136	4·84	·678		..
Bo. R........	136	95	·181	·0906	·0164	126	5·92	·808		..
Bo. R........	432	22	·223	·1025	·02286	91	6·16	·636		*A
Bo. R........	433	30	·260	·1140	·02962	72	7·50	·733		A
Bo. R........	106	155	·232	·0394	·00913	69	2·33	·259		..
Bo. R........	434	60†	·260	·0945	·02455	65	3·22	·497		A
Bo. R........	430	113	·197	·1160	·02285	45·2	3·21	·399		B
Bo. R........	103	135	·343	·0630	·0216	41·3	2·82	·216		..
P. D.	219	140	·232	·1045	·0244	35·5	2·64	·313		..
Bo. R........	429	120†	·492	·0945	·0464	31·6	4·71	·237		B
Bo. T. B....	412	120†	·473	·0513	·0243	17·4	1·43	·075		C
Bo. R........	413	250†	·256	·0513	·0131	35·5	1·1	·162		C

* See Table of Chemical Analysis *infra*. † Signifies that the steel was capable of further cutting.

About 250 trials were made; and a selection of the best results obtained is given in the following tables, in English units. These results have, as already mentioned, also been plotted, and smooth

BERLIN EXPERIMENTS.—*Continued.* TABLE II.—CAST IRON.

Brand of steel used.	Trial. No.	Duration. Minutes.	Cut. Inches.	Traverse. Inches.	Area of cut. Sq. ins.	Cutting speed. Ft. per min	Weight removed per min. lbs.	Surface machined per min. Sq. feet.	Skin or not.
Bo. R.	425	59‡	·1456	·1850	·0269	72·9	7·39	1·107	No
P. D.	515	61‡	·1870	·1692	·0316	50·3	5·21	·775	"
Bo. R.	424	120‡	·520	·1634	·0850	47·3	14·43	·710	"
Bo. R.	409	120‡	·579	·096	·0556	37·4	6·25	·291	"
Bg. St. I.	611	120‡	·559	·063	·0352	37·4	4·61	·226	"
P. D.	514	120‡	·520	·1417	·0737	35·4	7·39	·3875	"
P. D.	275	103‡	·300	·1437	·0431	35·4	5·65	·484	"
Bg. St. I.	633	30	·516	·1613	·0832	33·5	10·45	·538	"
Bg. St. I.	326	148‡	·396	·0867	·0343	33·5	4·31	·237	"
P. D.	273	190	·4375	·1043	·0456	27·6	5·74	·366	Skin

TABLE III.—CAST STEEL.

Brand of steel used.	Trial. No.	Duration. Minutes.	Cut. Inches.	Traverse. Inches.	Area of cut. Sq. ins.	Cutting speed. Ft. per min	Weight removed per min. lbs.	Surface machined per min. Sq. feet.	Skin or not.
Bo. R.	420	120‡	·2265	·067	·01517	47·3	2·457	·28	No
Bo. R.	419	120‡	·2166	·067	·01450	33·5	1·45	·189	"
P. D.	271	100‡	·590	·0275	·01622	31·55	2·346	·097	Skin
Bg. St. I.	624	120‡	·394	·0512	·02018	26·6	2·149	·1185	No
Bg. St. I.	328	133‡	·2205	·086	·01896	21·7	2·777	·151	"
Bg. St. I.	623	120‡	·610	·0512	·03122	19·71	2·149	·0862	"
Bg. St. I.	619	120	·630	·0512	·03225	18·72	2·071	·0754	Skin
Bo. R.	416	120	·630	·0492	·03100	17·73	2·115	·0862	"

‡ Signifies that the steel was capable of further cutting.

Brands of tool steel.
- Bg. St. I. = Bergische Stahl Industrie.
- Bo. T. B. = Böhler Titan Boreas.
- Bo. R. = Böhler Rapid.
- P. D. = Poldi Diamant ooo.
- P. S. = Poldi Schnelldreher.

curves drawn through them in Plate I. The three full-line curves indicate the speeds of cutting which were attained, for the various

sectional areas of cut, upon three kinds of Siemens-Martin steel, of which the ultimate strengths were 26 to 32 tons, 40¼ tons, and 49 tons per square inch respectively; their chemical composition being given in a subsequent table (VII.), where they are distinguished by the letters A, B, and C, in order named. The three curves marked S.F.P.S., M.F.P.S., and H.F.P.S., are those deduced from the Manchester experiments (described below), and are inserted here for comparison. It is probable that the softest English steel operated upon (Whitworth fluid-pressed) was much tougher than the softest Siemens-Martin steel employed at Berlin; it certainly was much more difficult to cut. The hardest German steel, on the other hand,

Variation of Cutting Speed with Area of Cut.
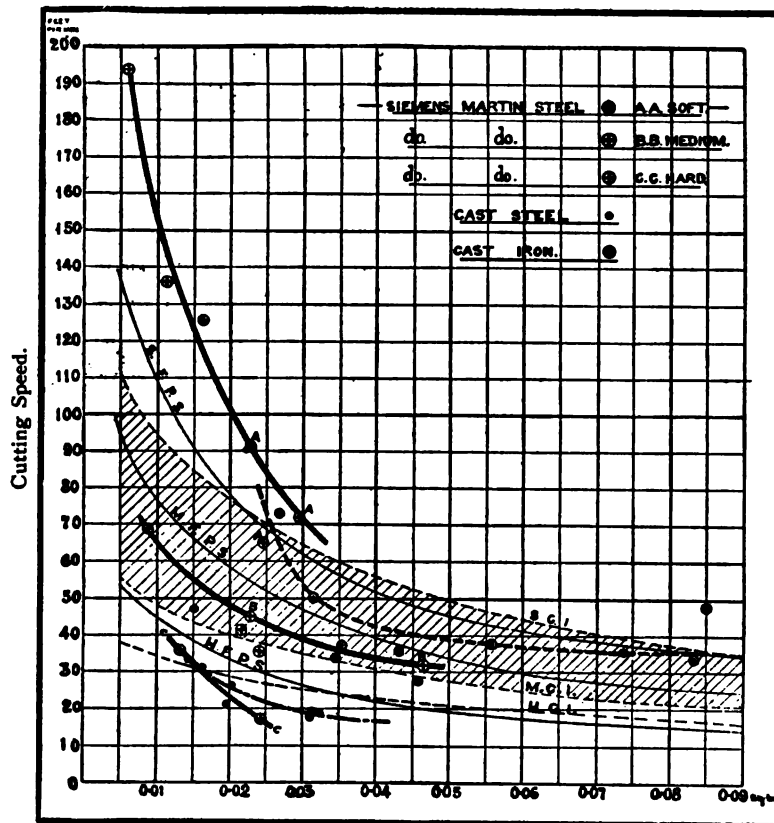
PLATE I.—AREA OF CUT—(CUT × TRAVERSE).
Comparison of Berlin and Manchester Experiments.

MANCHESTER EXPERIMENTS.—TABLE IV.

WEIGHTS REMOVED, AREAS MACHINED, AND CUTTING STRESSES.

Intended cut and traverse.		Actual area of cut.	Maximum speed of non-tailing tools.	Weight removed.	Area machined.	Average cutting stress.
Inches.		Square inches.	Feet per minute.	lbs. per minute.	Square feet per minute.	Tons per square inch
SOFT STEEL (WHITWORTH FLUID-PRESSED).						
1/16	1/16	·0032	149·2	1·72	·755	115
3/16	1/16	·0106	111·0	4·14	·575	
3/16	1/8	·0215	74·0	5·28	·756	
3/8	1/8	·0434	50·7	7·50	·511	
MEDIUM STEEL (WHITWORTH FLUID-PRESSED).						
1/16	1/16	·0039	105·2	1·50	·547	108
3/16	1/16	·0114	80·0	3·17	·417	
3/16	1/8	·0227	51·4	3·88	·539	
3/8	1/8	·0425	38·6	5·60	·403	
HARD STEEL (WHITWORTH FLUID-PRESSED).						
1/16	1/16	·0040	52·5	0·73	·273	150
3/16	1/16	·0124	41·2	1·71	·214	
3/16	1/8	·0219	30·8	2·30	·320	
3/8	1/8	·0452	20·2	3·10	·210	
SOFT CAST IRON.						
1/16	1/16	·0039	109·0	1·30	·567	51
3/16	1/16	·0124	99·5	3·60	·518	
3/16	1/8	·0214	66·2	4·38	·690	
3/8	1/8	·0459	55·5	7·46	·578	
MEDIUM CAST IRON.						
1/16	1/16	·0033	59·7	0·69	·308	84
3/16	1/16	·0115	49·0	1·73	·254	
3/16	1/8	·0227	33·1	2·23	·335	
3/8	1/8	·0446	24·3	3·32	·249	
HARD CAST IRON.						
1/16	1/16	·00375	38·5	0·48	·200	82
3/16	1/16	·01173	31·9	1·18	·167	
3/16	1/8	·02112	24·7	1·62	·257	
3/8	1/8	·04590	22·0	3·2	·230	

appears to have been more difficult to cut than the hard fluid-pressed steel used at Manchester. The spots *not* marked with the letters A, B, or C are of unknown tenacity. The thick-line-dotted curve gives the speeds and areas for the German experiments on cast iron, whose chemical analysis is recorded in Table (VII.). The thin-line-dotted curves, marked S C I, M C I, and H C I are the Manchester results for soft, medium, and hard cast iron; the region between the first two, in which the Berlin results fall, being hatched. Some valuable information regarding cast steel, deduced from the German records, is indicated by the dot-and-dash line in Plate I. No information regarding this material was obtained by the Manchester Committee.

THE MANCHESTER EXPERIMENTS.

A number of British firms have recently specialised in making rapid cutting steels, and it was with the object of testing the capabilities and commercial value of these brands that the experiments instituted

Variation of Cutting Force and Cutting Speed with area of Cut.
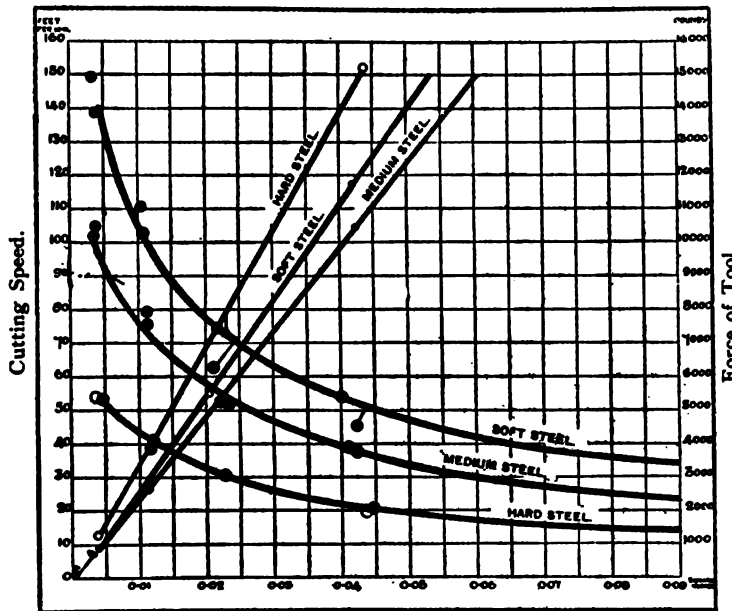
PLATE II.—AREA OF CUT—(CUT × TRAVERSE).

by the Manchester Association of Engineers were undertaken. The expense of these trials, which was not inconsiderable, was jointly borne by that Association, by the Municipal School of Technology of Manchester, and by the firm of Messrs. Sir W. G. Armstrong,

Whitworth and Company. The report upon them was presented at a meeting of the above Association held on October 24, 1903, and was published *in extenso* in *Engineering* of October 30 and November 6. This report, although confined strictly to an account of the mode of experimenting, of the results obtained, and of a few of the more obvious deductions from the latter, is a sufficiently lengthy production, containing, as it does, twenty-nine tables of figures and thirteen plates. It is an excellent example of the kind of work which the engineering colleges and the higher technical

Variation of Cutting Force and Cutting Speed with area of Cut.
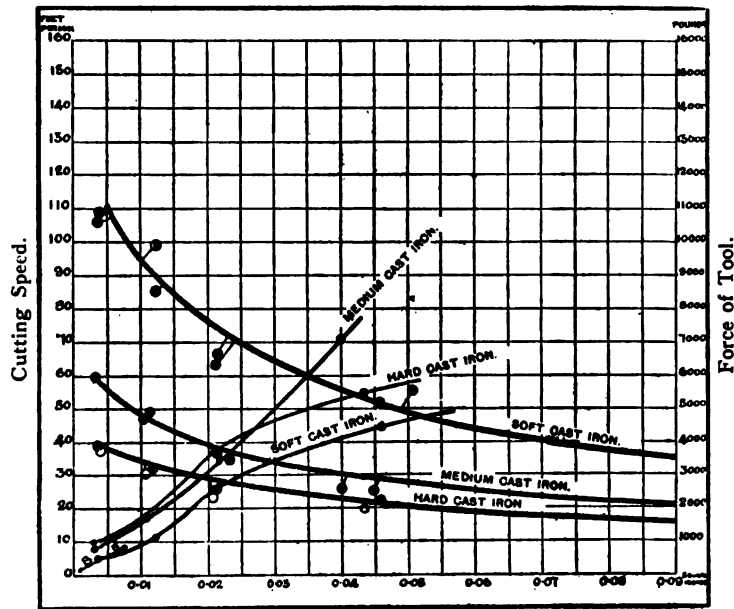
PLATE III.—AREA OF CUT—(CUT × TRAVERSE).

schools in this country ought to undertake, and must be prepared to perform, if they are to occupy the place of similar institutions abroad in the very important matter of practical research on current engineering questions. In carrying out the work here under discussion the Municipal School of Technology showed itself in the sphere of usefulness for which its engineering department, in a special sense, was primarily equipped, not merely as an institution for teaching young men the elements of engineering science, but also as an establishment where industrial experiments can be carried out on a practical scale. The planning, execution, and reporting of this

extensive series of trials is also a good instance of the results which can be attained by the united efforts of the educational and the industrial authorities. In carrying them out there have been combined the sound and discriminating common sense of the practising engineer, represented by such men as Mr. Daniel Adamson, Mr. H. N. Bickerton, Mr. E. G. Constantine, and Mr. George Daniels, who were the working members of the committee; the liberality of the renowned firm who provided the sinews of war, in the shape of twelve or fifteen tons of forgings and castings to be cut up; and, lastly, the trained staff and the facilities and instruments for experimenting which were available at the School of Technology.

The questions which the committee set themselves to answer in these trials may be shortly stated as follows :—(1) What maximum speeds can be obtained with the new steels when taking light or finishing cuts upon hard, medium and soft steel, and upon hard, medium and soft cast iron? (2) What maximum area of surface can be machined in a given time when taking a $\frac{3}{16}$-inch cut with the new steels upon the six given materials? (3) What is the greatest weight of cuttings which the new steels can remove in a given time from these three grades of steel and cast iron? (4) What forces are operative upon the tool in making these cuts, and according to what laws do these forces vary with the speed of cutting and the area and shape of the cut? (5) Can the new steels be forged and tempered by an ordinary smith, and yet be relied upon to give results as to cutting speed and durability similar to those obtained when they are delivered ready ground by the makers? The answers to the first four of these questions are contained in Table IV., abstracted from those of the report. This table is self-explanatory, and it need only be added that, as the cutting force was found to be closely proportional to the area of section of cut (*i.e.* product of actual cut and traverse), it is possible to give, as in the last column, the average cutting stress for each variety of steel or cast iron, irrespective of the size or shape of cut taken. One of the most noteworthy facts discovered is, that the cutting force does not increase, but appears rather to diminish, with increasing speeds. This is contrary to the opinion generally held by turners and machine-tool experts, as instanced by the objections raised by workmen to an increase of the cutting speed on account of the anticipated springing of the work. This objection will no longer hold good, for, although higher speeds of taking a given cut will, of course, require a greater driving power almost in direct proportion to the increased speed, no greater, but rather a smaller, force will be brought upon the tool; so that the load acting upon belts and gearing, and the tendency of the lathe and work to spring will be rather diminished (except for gapped work) than otherwise. On the other hand, it has been conclusively

shown by these trials that heavy cuts at moderately high speeds will remove much more material than light cuts at the highest possible speeds the tool can stand. For the cutting speed does not increase as fast as the area of the cut diminishes, so that more material can be machined off in a given time with a heavy cut than with a light

Diagram of Weights Removed and Cutting Speed on area of Cut.
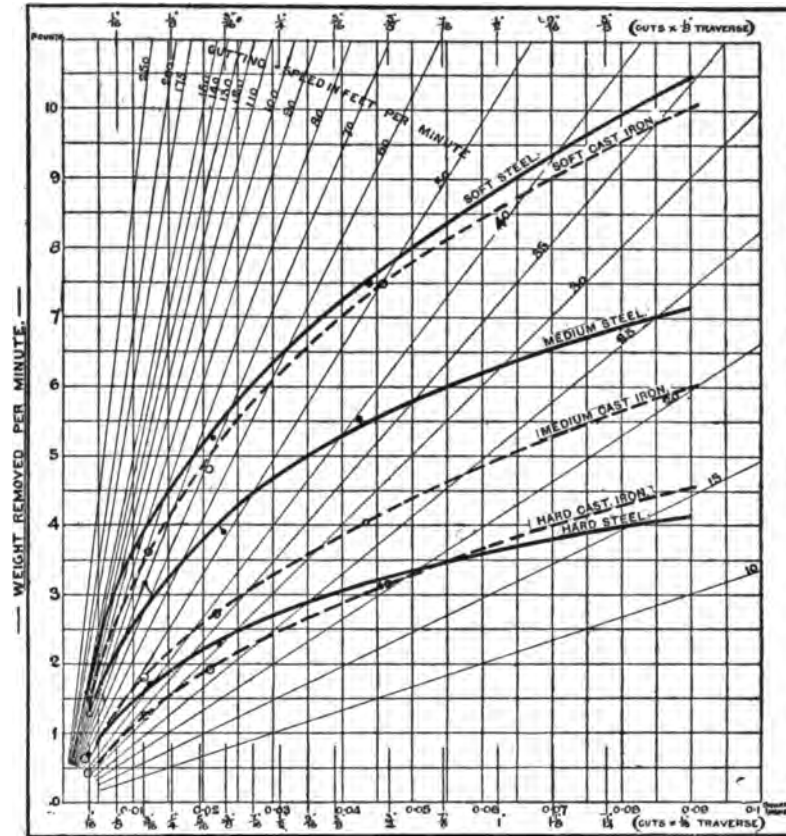
PLATE IV.—AREA OF CUT—(CUT × TRAVERSE).

cut at its corresponding faster speed. Further, the total or gross horse-power required for cutting consists of the sum of that lost by friction of the intermediate gearing and of the lathe, as well as the effective work spent upon cutting. Now the frictional or lost power does not vary much, whether there is a heavy or a light cut on the machine; it therefore forms a much larger percentage of the whole

at light cuts than at heavy cuts, and the latter are much more economical in power than the former.

The particular results of the Manchester experiments, which will probably prove to be most useful in practice, are those which indicate a law connecting the permissible speed of cutting with the product of depth of cut and width of traverse feed per revolution, or "area of cut." In endeavouring to give a simple expression to this law it has been found that a curve closely approximating to a rectangular hyperbola, with asymptotes parallel to the axes of speed and area of cut, can be drawn through the co-ordinates of the results obtained in the trials for each material. Such curves, with the actual spots of the trials to which they approach, are plotted in Plate II. for steel, and Plate III. for cast iron; and in each case for the three degrees of hardness of the material operated upon. The ordinates are speeds in feet per minute, the abscissæ areas of cut in square inches. The following form of expression gives the relations for all six cases :—

$$v = \frac{K}{a + L} + M$$

Where a is the area of cut in square inches, v is the allowable cutting speed in feet per minute, whilst K, L and M are constants, of which

CONSTANTS IN FORMULA FOR CUTTING SPEED.—Table V.

Constant.	Fluid-pressed Steel.			Cast-iron Bars.		
	Soft.	Medium.	Hard.	Soft.	Medium.	Hard.
K.........	1·95	1·85	1·03	3·10	1·65	1·30
L.........	·011	·016	0·16	·025	·030	·035
M.........	15	6	4	8	7	5·5

numerical values, for the various materials, are given in Table V. On the same diagrams, II. and III., are also plotted the lines showing the relation between the forces upon the tool required for cutting, and the areas of cut taken on the trials. These relations are linear for all the varieties of steel, but are of complex form for cast iron. The average values of the cutting force divided by area of cut are tabulated, for each material, on page 150 in the last column of the table there given. In Plate IV. are shown the curves approximating to the weights removed per minute in the Manchester experiments. The full lines are for steel, the dotted for cast iron. The spots give the actual results obtained, being the greatest weights removed by any non-failing tool, on each of the four series of trials made with the six samples operated upon. As ordinates we have lbs. removed per minute, as abscissæ area of cut (or depth of cut multiplied by

width of traverse). Since $W = \mu a v$, where μ is the density of the material, a the area of cut, v the speed, and W the lbs. removed per unit of time, we have $\dfrac{W}{a} = \mu v = \tan\alpha$, say. This means that if a sloping line be drawn through the origin of co-ordinates of the diagram of weights and cuts, making with the axis of areas an angle α, whose tangent is μ v, this sloping line will join points giving the weights

CHEMICAL COMPOSITION.—TABLE VI.

CAST IRON.

		Soft. *26·9 tons to the square inch.	Medium. 44 tons to the square inch.	Hard. 43·5 tons to the square inch.
	BERLIN.	MANCHESTER.		
Carbon (total) ...	3·91	...	...	...
Combined.........	0·45	0·459	0·585	1·150
Graphite	3·46	2·603	2·720	1·875
Silicon	2·05	3·010	1·703	1·789
Manganese	1·00	1·180	0·588	0·348
Sulphur	0·10	0·031	0·061	0·1614
Phosphorus	0·10	0·773	0·526	0·732

* Crushing strengths.

CHEMICAL COMPOSITION.—TABLE VII.

FORGED STEEL.

	SIEMENS-MARTIN.			WHITWORTH FLUID-PRESSED.		
	A †26 to 32 tons to the sq. inch.	B 40¼ tons to the sq. inch.	C 49 tons to the sq. inch.	Soft. †26·3 tons to the sq. inch.	Medium. 28·9 tons to the sq. inch.	Hard. 46·7 tons to the sq. inch.
	BERLIN.			MANCHESTER.		
Carbon	0·30	0·54	0·63	0·198	0·275	0·514
Silicon	0·05	0·21	0·20	0·055	0·086	0·111
Manganese ...	0·58	0·93	1·22	0·605	0·650	0·792
Sulphur	0·05	0·025	0·05	0·026	0·037	0·033
Phosphorus...	0·07	0·05	0·05	0·035	0·043	0·037

† Ultimate tensile strengths.

which will be removed for each cut at the given speed v (if this were a possible speed). Such sloping lines will in fact be (contour) lines of constant speed, and are a useful addition to the diagram of weights removed. Thus, e.g., if we wish to know at what speed 5 lbs. per minute can be removed, we can tell at a glance by running across the diagram upon the 5 lbs. line that the speed would have

to be 200ft. per minute for a $\frac{1}{8}''$ by $\frac{1}{16}''$ cut (0·00391 area), 96ft. per minute for a $\frac{1}{4}''$ by $\frac{1}{8}''$ cut (0·0156 area), and 33ft. per minute for a $\frac{3}{8}''$ by $\frac{1}{8}''$ cut (0·047 area). The first speed is impossible on materials operated on, the second is problematic, and the third could only be taken upon the milder varieties of steel. Or, conversely, we can tell the weights which will be removed if we run at a given speed on a given material; also the depth of cut and width of traverse we may safely employ. The following Tables (VI. and VII.) give particulars of chemical composition and ultimate strength of materials operated upon both in the Berlin and Manchester experiments. A few words may, in conclusion, be added regarding the explanations offered by chemists of the extraordinary efficiency and durability, under high temperatures, of the new steels. A series of systematic experiments, carried out in the works of the Poldihütte Company, have led to the following enunciation of the matter (see *Stahl und Eisen*, April 15, 1902). The carbon in the air-hardening steels forms carbides, not only with the iron, but also with the other metals, such as chromium, tungsten, etc., which they contain. The iron carbides are as a rule in the unhardened state, whilst at certain higher temperatures the iron has the property of giving off the carbon, which then shows a greater affinity for chromium and tungsten, forming carbides with them. These metallic carbides are fixed by rapid cooling; and, as they possess the property of hardness to an extraordinary degree, they are able to impart this to the steel into whose composition they have entered. Also this hardness is retained when the steel is much heated, for the new carbides are not altered by temperature, except beyond certain limits. This constitutes the radical difference between self-hardening and pure carbon steels. With the latter the hardness, due to the well-known combination of the carbon and iron, is lost after a small amount of heating. With the former the steel may be very considerably heated without losing its hardness, *i.e.*, its cutting properties. The limits which may be reached without injury depend, not only on the total percentage content of carbon and metals, but also upon the proportion of the former to the latter. The matter may perhaps be roughly generalised as follows :—Combined carbon gives hardness, whether it be in the form of iron, chromium, tungsten, or other metallic carbide. Mechanically mixed carbon does not increase the natural hardness of iron. Thus white or hard cast irons contain $2\frac{1}{2}$ per cent. of combined carbon and less than 1 per cent. of graphite, whilst soft or grey cast iron contains only 1 per cent of combined carbon to $2\frac{1}{2}$ per cent of graphite. In hard carbon steel the greater proportion of the carbon is present in combination with the iron, whilst in the soft variety the greater part seems to be in intimate mechanical mixture with the iron, for it is left undissolved

on treating the steel with an acid. In the case of either the cast iron or the carbon steel, rapid cooling promotes or maintains chemical combination, whilst slow cooling allows the carbon to crystallise out. In steels in which chromium, tungsten, etc., are present, the carbon deserts the iron and clings to these other metals at high temperatures, such as 2000° Fahrenheit, and when the steel is cooled at such comparatively slow rates as occur in an air-blast these metallic carbides are not broken up, and the steel remains hard. These carbides also possess a very much greater hardness than the iron carbide, and are only decomposed at very much higher temperatures than those at which the latter breaks down.

Some Experiments for Determining
the elastic and ultimate strength of brickwork piers and pillars of Portland-cement concrete.

By W. C. POPPLEWELL, M.Sc., Assoc. M. Inst. C.E.

THE experiments described in this paper formed part of a series of tests carried out by the Author and his students upon samples of brick, mortar, brickwork, concrete, and ferro-concrete. Experiments upon the larger specimens, including the brickwork piers and the specimens of concrete and ferro-concrete, were carried out in the vertical 750-ton compression testing machine in the Materials Testing Laboratory at the Municipal School of Technology, Manchester. The elastic tests of the smaller specimens, such as individual bricks, cubes of mortar and cement, were made in the 50-ton Wicksteed testing-machine in use in that laboratory.

Setting the Specimens in the Machines. Some of the brickwork columns were built in position, ready for testing, on the lower platen of the testing-machine, whilst others were built outside the machine, on rigid square frames of timber, and were moved bodily into the machine after the proper interval of time had elapsed. Each specimen was first set vertically on the lower platen in a thin layer of neat cement. The upper surface, which had been left approximately true by the maker, was then covered with a thin layer of cement, and the upper platen brought down upon it with just sufficient force to render the top surface true. Before bringing down the table a thin sheet of greased millboard was interposed between the metal and the cement to prevent the latter from adhering to the platen, and at the same time to assist in equalising the stress on the specimen. The specimens of concrete and mortar, as well as the bricks, were set in quick-setting plaster of Paris. Both these methods of bedding were found to give fairly uniform distribution of the stress.

Measurement of the Compressive Strains. In nearly all the tests recorded in this paper the compressions of the specimens due to the loads imposed were observed and measured by means of the Martens mirror extensometer. The arrangement adopted for measuring the strains in a brick column by means of this instrument is shown in Fig. 1. Two rigid bars, *a* and *b*, are held in position, against the front and back of the column respectively, by means of light springs. Each of these bars carries at its lower end, and rigidly attached to it, a circular knife-edge, which is pressed against the material of the specimen by the spring. The upper end of each bar is provided with a groove, in which rests one edge of a short prism, *c*, of hardened steel, having a diamond-shaped section, and the other edge of this prism or double knife-edge is held by the pressure of the spring-clip against the surface of the specimen. The measuring-bars, *a* and *b*,

when adjusted in their proper positions, lie parallel to the axis of the specimen, and a plane containing the two edges of the rocking-prism, c, should be approximately normal to the axis of the specimen. At the end of an axial extension of the rocking-prism is carried a small plane mirror, d, which is capable of rotation about either of two axes at right angles, one of which is the axis of the prism. Two telescopes, one for each mirror, are carried on a tripod t, and to each of these is attached a scale s. The diaphragm of each telescope is fitted with a horizontal cross-wire. When the instrument has been finally adjusted, each scale is observed through a telescope, its image being reflected from the face of the corresponding mirror; the cross-wire in the diaphragm of the telescope appears to lie across the
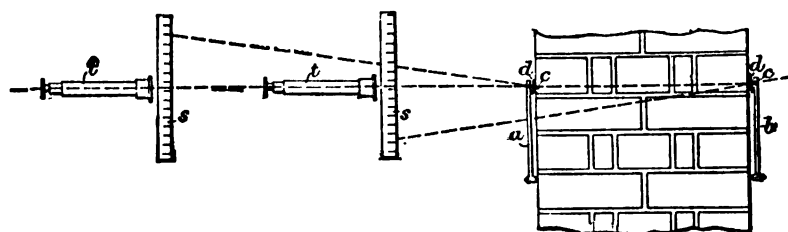
Fig. 1.

scale, and the reading given by this cross-wire on the scale provides a measure of the compression of the specimen. As the load on the specimen increases, the distance between the two points of contact, namely, the sharp edge of the disk at the lower end of the measuring-bar, and the edge of the rocking-prism which touches the surface of the material, diminishes, with the result that the prism, and consequently the mirror which it carries, becomes tilted through a small angle, and a different part of the scale is seen reflected from it on looking through the telescope. In this way the apparent movement of the hair-line along the image of the scale becomes a measure of any variation in the length of the measured portion of the specimen. In the particular case in question the arm of the optical lever, or the distance between the face of the mirror and the scale, is so chosen that the numbered divisions on the scale correspond to length-variations of thousandths of an inch. Each of these numbered divisions is actually 1 centimetre in length, and is divided into millimetres. These millimetre divisions thus correspond to ten-thousandths of an inch variation in the length of the specimen, and as it is possible to subdivide these into fifths with a fair degree of certainty, length-variations of the specimen can be read to within one fifty-thousandth of an inch. This instrument can be applied to almost any kind of test-specimen, as well as to parts of structures

and machines in actual use; its readings are very clear and distinct, and at the same time a high degree of precision is attained. It is not suitable for rapid work, as the setting and adjustment take some little time to effect.

Method of carrying out the Experiments. In nearly every case the method of carrying out an experiment was as follows :—After the bedding had been completed, and before the commencement of the experiment, the Martens mirrors were fixed on the specimen and carefully adjusted. Loads were then imposed, by uniform increments, and readings were taken on the front and back mirrors after each increment of load. Before reaching the elastic limit of the material the load was removed and the permanent set, if any, was noted. This process was repeated until several sets of readings had been obtained. Then, for the final set of readings, the loadings were continued until the material began to crack, or until the cross-wire of the telescope got beyond the end of the scale. When this point had been reached the mirrors were removed and the specimen was tested to destruction by gradually increasing the load.

Results of the Experiments. The results of the experiments are numbered Nos. 1 to 24 inclusive. These numbers refer in most cases to individual experiments; in one or two instances groups of experiments are referred to. Stress-strain curves have been plotted from the results of the experiments, the stresses being given in tons per square foot and the strains in thousandths of an inch on 12 inches length of the specimen. For purposes of comparison the same scale has been used throughout, as far as possible. In some cases curves have been plotted from all the sets of readings obtained, separate curves being plotted for the readings taken on the front and back faces of the specimen, and also for the means of the front and back readings. The readings taken on the front face are indicated by small open circles, whilst those taken on the back face are denoted by circular black spots, the mean curve being shown without any indication of the individual points. For the remaining experiments only the mean curves are given.

Limit of Proportionality. For nearly all the materials experimented upon, the compressions were found to be sensibly proportional to the corresponding stresses during the earlier stages of the loading. This is clearly shown by the plotted diagrams. It will be seen that for a considerable period after the commencement of the loading the plotted points lie on a straight line. The point in the loading at which the line ceases to be straight and curvature begins may be taken as the "limit of proportionality." It will be observed that this limit is raised to a higher point after the first loading.

Modulus of Elasticity. The value of the elastic modulus or coefficient has been calculated in the usual way, the stresses (S) taken being the differences between upper and lower limits of stress within the limit of proportionality, and as far apart as possible. The corresponding strains (X) were taken as the number of thousandths of an inch compression on a length of 12 inches. Where readings were taken on both front and back faces of the specimen, the mean reading was taken. In the actual experiments measuring-bars of various lengths were used to suit the dimensions of the individual specimens, but for convenience in comparison the author has reduced all the readings of compression to their equivalents for a uniform measured length of 12 inches. Calculating from these stresses and strains, the elastic modulus becomes :—

$$E = \frac{12,000\ S}{X}\ \text{tons per square foot.}$$

The coefficient so obtained is the ordinary coefficient, or Young's modulus, E, as distinguished from what Unwin calls E^1, which is calculated from strains after the permanent portion or "set" has been as far as possible eliminated. From some of the experiments described several different values of the modulus have been obtained, these values corresponding to the different successive loadings. It will be noticed that the permanent set is reduced with each successive loading—this reduction being most marked after the first loading—with the result that the modulus increases with each successive loading. This is not strictly true for every experiment in which several sets of readings have been taken, but it represents the general tendency. How far this reduction of set and increase of modulus might be carried by an indefinite number of successive loadings with relatively high stresses it is impossible to foretell, but the experiments appear to show that after two or three repetitions the strains become practically constant.

The Cracking-Stress. On examining the curves it will be seen that with each successive loading the total strain corresponding to a given stress is reduced, this being probably due to a squeezing together and closing up of the interstices in the material. During the last loading previous to final destruction a point is always reached at which slight cracks begin to appear on the surface of the specimen. In most cases it was found that a warning of the approach of this point was given by slight creaking sounds being heard before any cracks could be actually seen. The load at which this cracking was first detected has been called the "cracking-load," and from it is calculated the "cracking-stress." Usually very few strain measurements were possible after the cracking-load had been passed, the loads being gradually increased until a maximum was reached

beyond which the load could no longer be supported by the specimen. This has been called the "crushing-load," and from it the "crushing-stress" has been calculated. A peculiarity of the plain concrete pillars tested is that they invariably failed completely at the cracking-load. In other words, the specimen collapsed on the first appearance of the minutest crack. The following are the detailed results :—

No. 1. Pier of common wire-cut bricks set in lime-mortar (2 parts sand to 1 part lime), tested 4 weeks after building. Dimensions of pier : 1 foot 6 inches by 1 foot 6 inches, by 3 feet in height.

RESULTS.

Began to crack with stress of 35·00 tons per square foot.
Badly cracked   "   "   47·50   "   "   "
Crushed   "   "   53·00   "   "   "
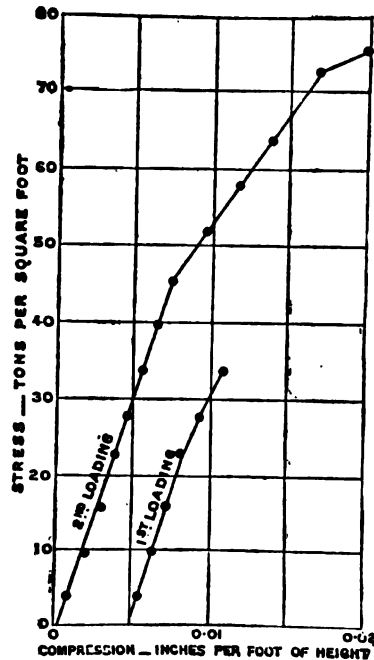
Fig. 2.

With this specimen no attempt was made to take any measurements of the elastic compressions, and the results yielded are simply those of a pier of the most ordinary soft bricks set in lime-mortar, and tested only 4 weeks after building.

No. 2 (Fig. 2):—Pier of common wire-cut bricks set in Portland-cement mortar (3 parts sand to 1 part cement), tested 39 weeks after building. Dimensions of pier : 1 foot 6¼ inches by 1 foot 6⅜ inches, by 3 feet in height. Martens mirrors set on back surface of pier. Measured length, 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—	Lbs. per square inch.		Tons per square foot.
First loading, up to 40 tons per square foot......	1,276,000	...	82,000
Second „ „ „ „	1,400,000	...	90,000

First crack at 63·70 tons per square foot
Crushed „ 84·30 „ „ „

When readings are taken on one face only, as in this case, there arises a possibility of error in the calculation of the modulus. The compressions as given by readings taken on one face of the specimen may or may not be the average strains. In most cases there is at
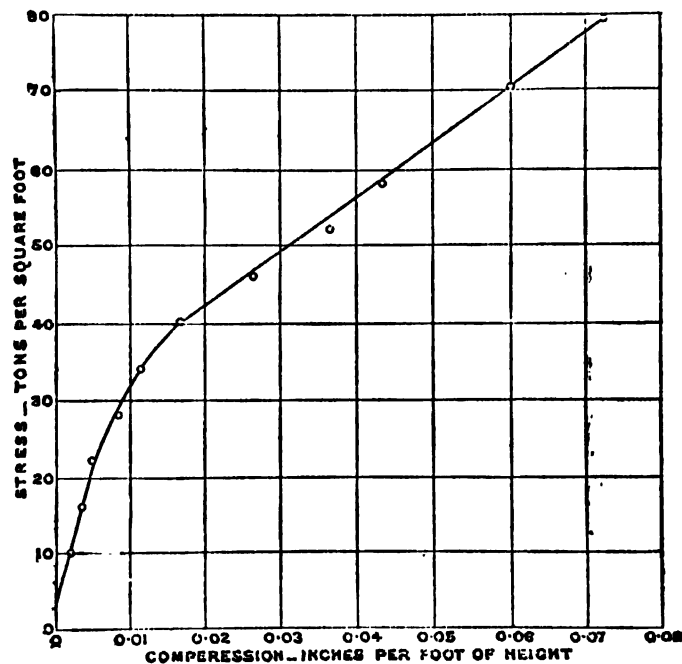
Fig. 3.

least some variation between the compressions on opposite faces. In the present instance it has been necessary to assume the compression to be uniform and equal to that at the back face. That this

assumption is within certain limits justifiable is shown by an inspection of the pairs of curves plotted from the experiments in which both mirrors were used.

No. 3 (Fig. 3):—Pier of Accrington (Huncoat plastic) bricks in black lime mortar, tested 4 weeks after building. Dimensions: 1 foot 6¼ inches by 1 foot 6¼ inches, by 3 feet in height.

RESULTS.

Elastic modulus—

    [800,000] lbs. per square inch.   [51,400] tons per square foot.

                Cracked at 78·30 tons per square foot.
                Crushed „ 95.50   „   „   „

The measurements of compressions were in this case taken on the whole length, and included the compression of the cement bedding at the ends. This measurement was effected by reading through a microscope attached to the lower platen on to a finely-divided steel
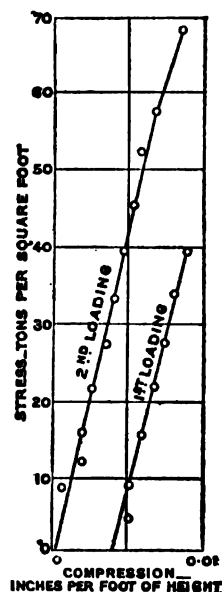
Fig. 4.

scale attached to the upper platen of the testing-machine. The elastic modulus arrived at is an illusory quantity, because the compressions measured are not those of the brickwork alone, but include the compressions of the packing or setting material at the ends of the pier. The compression of this packing material is

relatively greater than that of the brickwork alone, with the result that the strains used in calculating the modulus are too great, and the modulus is too small.

No. 4 (Fig. 4):—Pier of blue Staffordshire bricks set in Portland-cement mortar (3 parts sand to 1 part cement), tested 39 weeks after building. Dimensions: 1 foot 6¼ inches by 1 foot 6¼ inches, by 3 feet in height. Martens mirrors set on front face of pier. Length of measured portion, 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—		Lbs. per square inch.	Tons per square foot.
First loading, up to 40 tons per square foot......		1,420,000 ...	91,300
Second „ 30 „ „		1,470,000 ...	94,500
„ „ 30 to 35 „ „		1,880,000 ...	121,000
Cracked at 69·10 tons per square foot.			
Crushed „ 97·70 „ „ „			
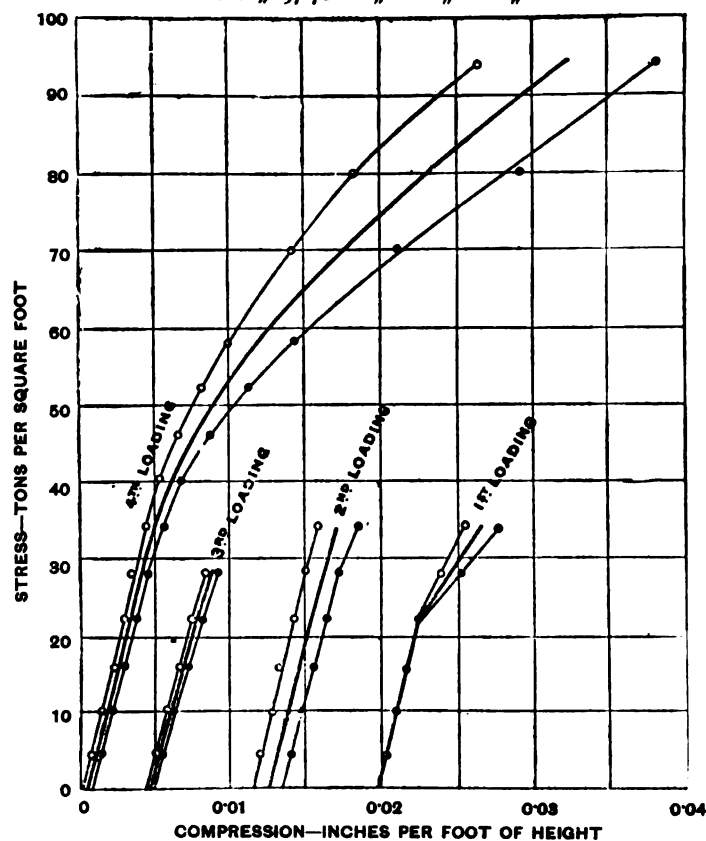
Fig. 5.
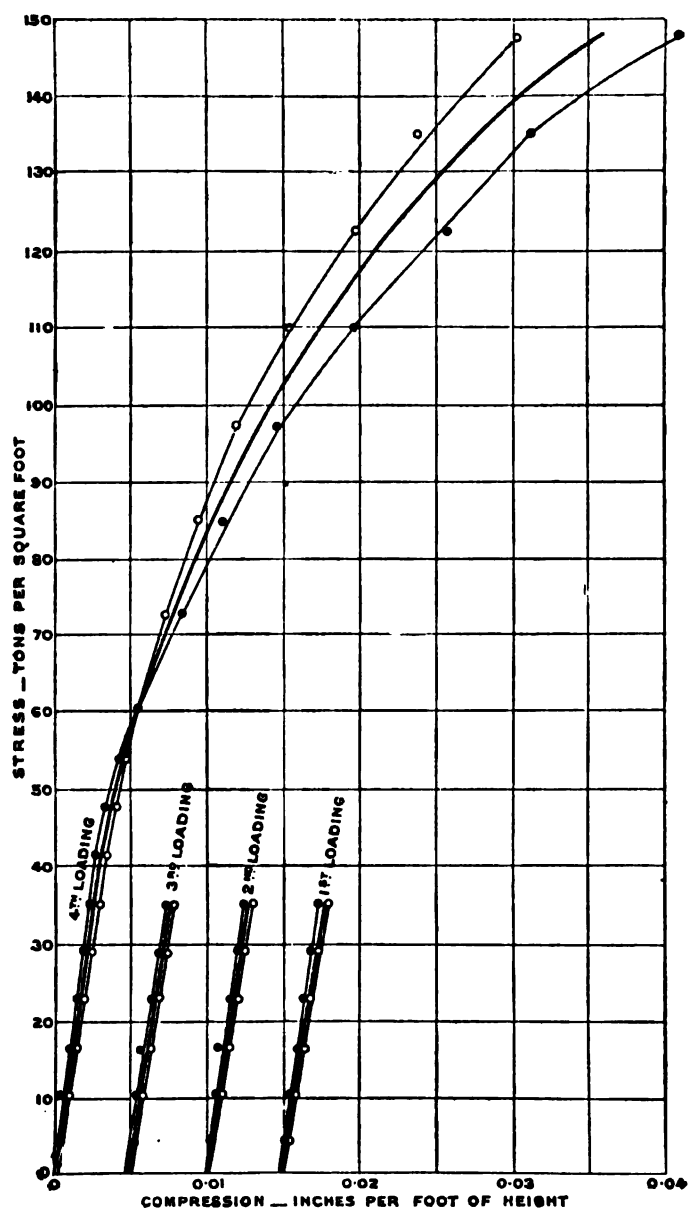
Fig. 6.

No. 5 (Fig. 5):—Pier of brindle-bricks set in black lime-mortar, tested 12 weeks after building. Dimensions: 1 foot 6¾ inches by 1 foot 6¼ inches, by 2 feet 11 inches in height. Martens mirrors set on both front and back faces of pier. Measured length, 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—

					Lbs. per square inch.		Tons per square foot.
First loading, up to 22 tons per square foot				......	1,360,000	...	87,400
Second	„	34	„	„	......	1,350,000	... 86,800
Third	„	22	„	„	......	1,350,000	... 86,800
Fourth	„	28	„	„	......	1,520,000	... 97,700

Cracked at 100·00 tons per square foot.
Crushed „ 164·60 „ „ „

This was the first of a set of six piers, built in pairs, of the same kind of bricks but with three different kinds of mortar. The three kinds of mortar used were black lime-mortar, composed of lime,
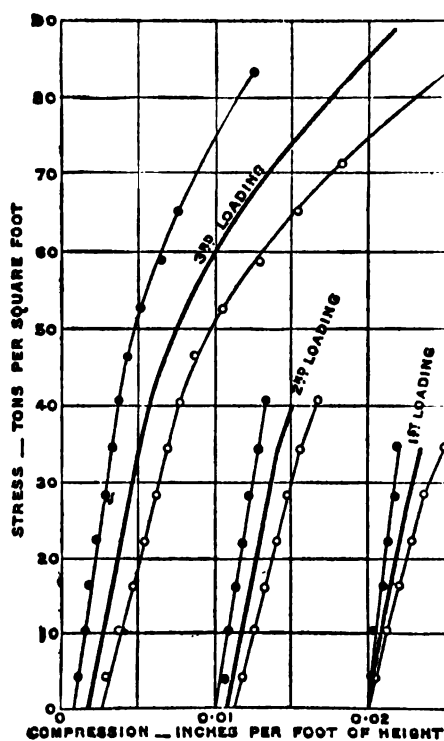
Fig. 7.

sand, and ground cinder; Portland-cement mortar, made with 3 parts of sand to 1 part of cement; and Lias-lime mortar, composed of Lias-lime and sand. The piers were tested in two sets of three piers each, made with the three mortars, at intervals of approximately 3 months and 6 months after building. All four piers built with lime-mortar and cement-mortar gave excellent results, but those built with Lias-lime mortar were less satisfactory; this is probably accounted for by the bricklayer having mixed the mortar too long before it was to be used, with the result that it must have been partially set before it was laid on the bricks. Nos. 6, 7, 8, 9 and 10 form the remaining piers of the same series.
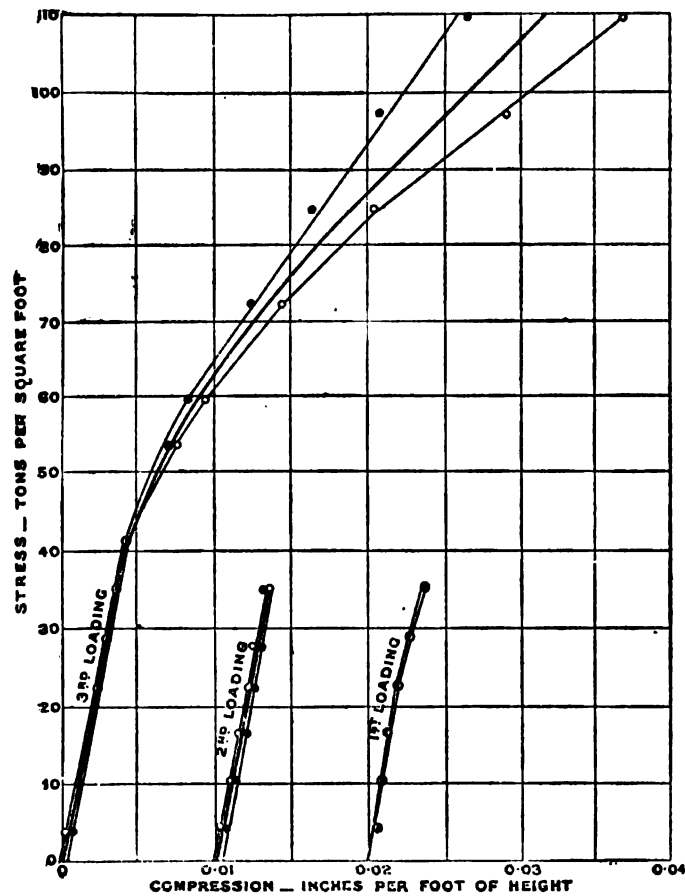
Fig. 8.

No. 6 (Fig. 6) :—Brindle-brick pier set in black lime-mortar, tested 25½ weeks after building. Dimensions : 1 foot 6 inches by 1 foot 5⅜ inches, by 2 feet 11 inches in height. Martens mirrors set on both faces of the pillar. Measured length 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—	Lbs. per square inch.	Tons per square foot.
First loading, up to 28·97 tons per square foot...	2,605,000 ...	167,500
Second „ „ „ „ „ ...	2,508,000 ...	161,200
Third „ „ „ „ „ ...	2,520,000 ...	162,000
Fourth „ „ „ „ „ ...	2,330,000 ...	149,800

Slight crack heard at 109·70 tons per square foot.
Cracked throughout „ 147·20   „   „   „
Crushed at 185·00 tons per square foot.

No. 7 (Fig. 7) :—Brindle-brick pier set in Portland-cement mortar (3 to 1), tested 12 weeks after building. Dimensions : 1 foot 6⅛ inches by 1 foot 6 inches, by 2 feet 11 inches in height. Martens mirrors set on both front and back faces. Measured length, 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—	Lbs. per square inch.	Tons per square foot.
First loading, up to 16·26 tons per square foot...	1,940,000 ...	125,000
Second „ „ 28·45 „ „ „ ...	1,930,000 ...	124,000
Third „ „ 40·70 „ „ „ ...	1,880,000 ...	121,000

Cracked at 132·00 tons per square foot.
Crushed „ 169·00   „   „   „

No. 8 (Fig. 8) :—Brindle-brick pier set in Portland-cement mortar, tested 26 weeks after building. Dimensions : 1 foot 6 inches by 1 foot 6 inches, by 2 feet 11 inches in height. Martens mirrors set on both front and back faces of the pier. Measured length, 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—	Lbs. per square inch.	Tons per square foot.
First loading, up to 28·81 tons per square foot...	1,980,000 ...	127,000
Second „ „ 28·81 „ „ „ ...	2,050,000 ...	132,000
Third „ „ 41·25 „ „ „ ...	1,895,000 ...	122,000

Began to crack at 90·20 tons per square foot.
Crushed at 161·30 tons per square foot.
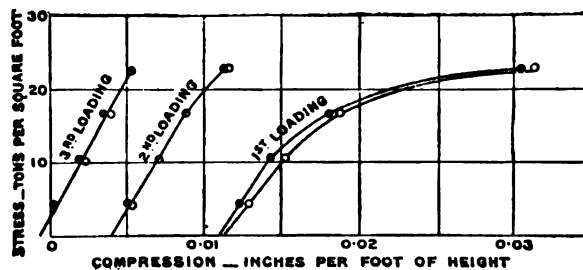
Fig. 9.

No. 9 (Fig. 9) :—Brindle-brick pier set in Lias-lime mortar, tested 12 weeks after building. Dimensions : 1 foot 6⅛ inches by 1 foot 5¾ inches, by 2 feet 11 inches in height. Martens mirrors set on both front and back faces of the pier. Measured length, 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—		Lbs. per square inch.	Tons per square foot.
First loading, up to 10·25 tons per square foot......		543,000 ...	34,900
Second „ „ 16·48 „ „ „		624,000 ...	40,100
Third „ „ 23·60 „ „ „		688,000 ...	44,200

Began to crack at 38·10 tons per square foot.
Crushed at 118·70 tons per square foot.

COMPRESSION — INCHES PER FOOT OF HEIGHT
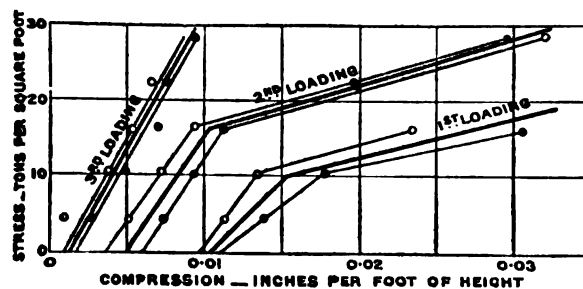
Fig. 10.

No. 10 (Fig. 10) :—Brindle-brick pier set in Lias-lime mortar, tested 26 weeks after building. Dimensions : 1 foot 6 inches by 1 foot 6¼ inches, by 2 feet 11 inches in height. Martens mirrors set on both front and back faces of the pier. Measured length, 20 centimetres (7·88 inches).

RESULTS.

Elastic modulus—		Lbs. per square inch.	Tons per square foot.
First loading, up to 10·15 tons per square foot......		396,000 ...	25,500
Second „ „ 16·25 „ „ „		598,000 ...	38,500
Third „ „ 28·50 „ „ „		638,000 ...	41,000

Cracked at 40·70 tons per square foot.
Crushed „ 101·70 „ „ „

All the brickwork piers experimented upon in the foregoing tests (Nos. 1 to 10) were built by working bricklayers, who freely used their own discretion as to the bond and other details of construction. This was done so that the work might be as nearly as possible the kind of brickwork usually met with in ordinary engineering practice. The actual bond used was in the main that shown in Fig. 11.

The results of the tests of brickwork piers are summarised in the following table :—

No.	Kind of Bricks.	Kind of Mortar.	Weeks after building	Appr'xi-mate limit of Propor-tionality	Crack-ing Stress,	Crush-ing Stress,	Elastic Modulus.	
				Tons per sq. ft	Tons per s. ft.	Tons per s. ft.	Tons per sq. foot.	Lbs. per sq. inch.
1	Common wire-cut	Lime	4	—	35	53	—	—
2	Common wire-cut	Portland-cement	39	25	64	84 {	82,000 / 90,000	1,276,000 / 1,400,000
3	Accrington	Black lime	4	24	78	96	(51,400)	(800,000)
4	Blue Staffordshire	Portland-cement	39	55	69	98 {	91,300 / 94,500 / 121,000	1,420,000 / 1,470,000 / 1,880,000
5	Brindle	Black lime	12	22	100	165 {	87,400 / 86,800 / 86,800 / 97,000	1,360,000 / 1,350,000 / 1,350,000 / 1,520,000
6	„	„	25½	40	110	185 {	167,500 / 161,200 / 162,000 / 149,800	2,605,000 / 2,508,000 / 2,520,000 / 2,330,000
7	„	{ Portland-cement	12	35	132	169 {	125,000 / 124,000 / 121,000	1,940,000 / 1,930,000 / 1,880,000
8	„	„	26	30	90	161 {	127,000 / 132,000 / 122,000	1,980,000 / 2,050,000 / 1,895,000
9	„	Lias-lime	12	10	38	119 {	34,900 / 40,100 / 44,200	543,000 / 624,000 / 688,000
10	„	„	26	10	41	102 {	25,500 / 38,500 / 41,000	396,000 / 598,000 / 638,000

1, 7.
3, 5, (7), 9, 11.

FRONT
FRONT

FRONT
FRONT

2, (4), 6, 8, (10),
4, 10.

Fig. 11.

Nos. 11, 12, 13 and 14 (Fig. 12) :—Single bricks, similar to those used in the construction of the piers. The elastic tests were made with the bricks placed on end, with the Martens mirrors attached. The crushing tests were made with the bricks set on their proper beds in plaster-of-Paris. The curves plotted in Fig. 12 refer to the
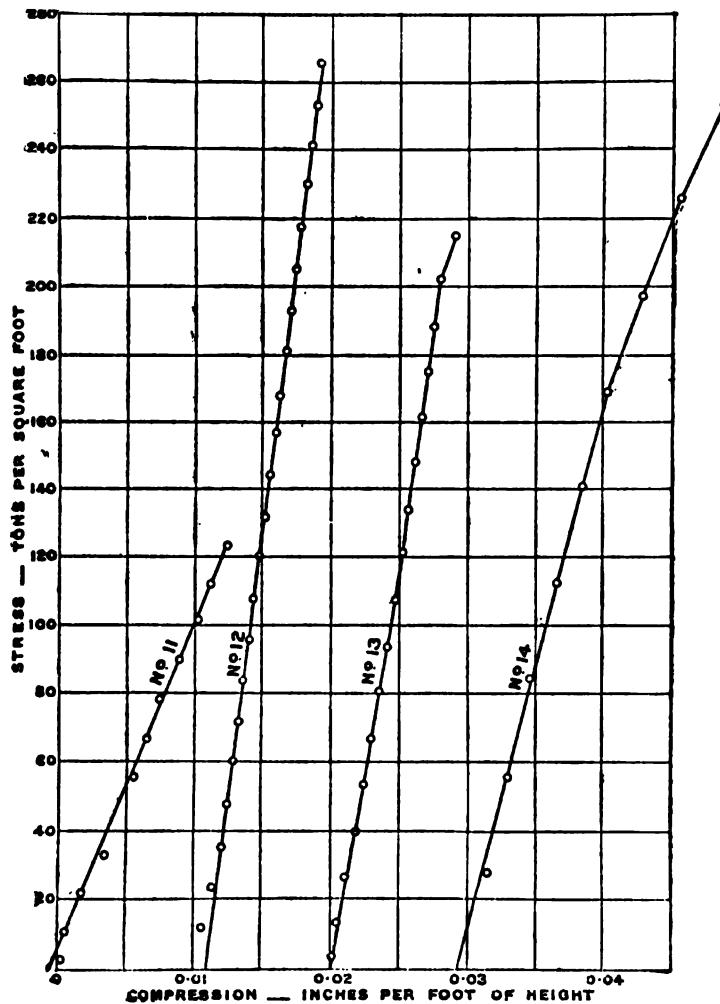
Fig. 12.

four kinds of bricks tested. The principal results obtained from these tests are given together in the following table :—

No.	Kind of Brick.	Dimensions.	Elastic Modulus.	Cracking Stress.	Crushing Stress.
		Inches.	Lbs. per square inch.	Tons per sq. foot.	Tons per sq. foot.
11	Common wire-cut (Manchester)...	} $8\frac{3}{4} \times 4\frac{3}{8} \times 3$	1,760,000	87	264
12	Accrington (Huncoat Plastic)...	} $8\frac{3}{4} \times 4\frac{3}{8} \times 3$ {	3,160,000 (up to 36 tons per sq. foot). 5,920,000 (from 36 tons to 200 tons per sq. foot).	} 118 {	250 (mean of three tests)
13	Blue Staffordshire ...	$9 \times 4\frac{1}{2} \times 3$ {	4,430,000 (0 to 100) 5,280,000 (100 to 200)	} 82	356
14	Blue Brindle (Staffordshire)...	} $8\frac{7}{8} \times 4\frac{1}{4} \times 3$ {	2,830,000 (up to 160 tons per sq. foot)	204 (mean of nine tests)	485 (mean of nine tests)

Nos. 15 and 16 (Fig. 13) :—Cubes made from the lime-mortar and cement-mortar used in building the piers. These experiments are not satisfactory, as the results of tests of cubes of a mortar are not comparable with the results of loading the same material when used to form the joints of brickwork, except perhaps as regards the
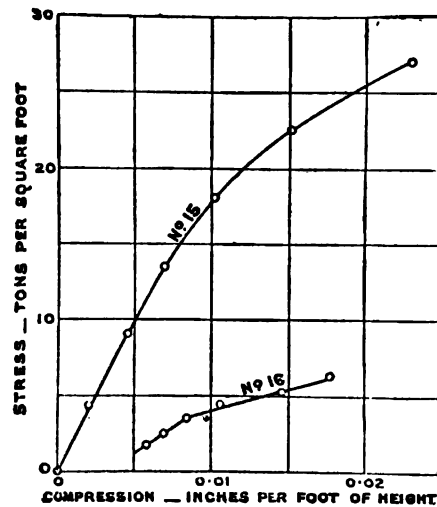
Fig. 13.

elastic modulus. This is not only by reason of the difference in dimensions, but also because the material resulting from setting in the form of a relatively large cube under no pressure is not the same as that obtained from the setting which takes place in thin layers between bricks under some small pressure. The curves obtained from these experiments are shown in Fig. 13, and the results are summarised in the following table :—

No.	Composition.	Dimensions.	Elastic Modulus.	Cracking Stress.	Crushing Stress.
		Inches	Lbs. per square inch.	Tons per sq. foot.	Tons per sq. foot.
15	Black lime-mortar (lime, sand, ground cinder), 28 w'ks old	4 × 4 × 4	352.000	31·8	31·8
16	P'rtl'nd-cem'nt mortar (3 sand and 1 cement) 24 w'ks old	4 × 4 × 4	131,500	10·0	10.0

Nos. 17 to 24 (Fig. 14) :—Cubes and columns of Portland-cement concrete, and pillars of reinforced concrete. The curves obtained are shown in Fig. 14, and the principal results are given below :—

No.	Material.	Age, Weeks.	Appr'ximate Limit of Proportionality	Cracking Stress.	Crushing Stress.	Elastic Modulus.	
			Tons per sq. ft	Tons per sq. ft	Tons per sq. ft	Tons per square foot.	Lbs. per square inch.
17	Concrete cube, dock gravel and finely-ground cement (5 to 1)	13	65	183	211	105,000	1,633,000
18	Concrete cube; dock gravel & ordinary cement (5 to 1)	34	95	196	225	164,000	2,550,000
19	Concrete column; dock gravel and ordinary cement (5 to 1)	15	40	70	70	113,000	1,750,000
20	Ditto	27	40	101	101	118,000	1,830,000
21	Concrete column; broken sandstone and Portland cement (5 to 1)	53	75	141	141	99,000 / 120,000	1,540,000 / 1,860,000
22	Reinforced concrete col'mn; dock gr'vel & ordinary cement (5 to 1)	15	140	120	210	113,000 / 142,000	1,760,000 / 2,210,000
23	Ditto	27	109	211	236	169,000	2,630,000
24	Concrete same as No. 21. Transverse links twisted	53	190	211	343	307,000 (mean of five tests)	4,780,000 (mean of five tests)

Of these, Nos. 17, 18, 19, 20, 22 and 23 are experiments taken from a series carried out by the author in connection with the construction of the new storage sheds for the most recently constructed of the docks for the Manchester Ship Canal Company. The sheds are constructed on the Hennebique reinforced concrete system. Nos. 21 and 24 are respectively a plain concrete and a ferro-concrete column formed of the material used in the construction of a highway bridge in Rochdale, on the Hennebique system. The material of these specimens of concrete and ferro-concrete varies in respect of
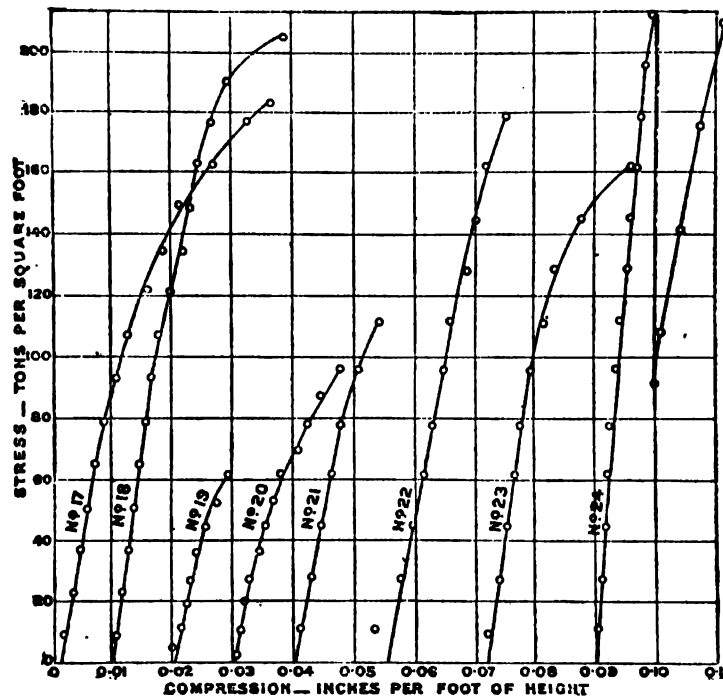
Fig. 14.

both the kind of ballast used and the make of the cement. In all cases the ballast was sufficiently small to pass through a ½-inch or ¾-inch mesh, and was in some cases pebbly gravel and sand obtained in excavation for the dock, while in others it consisted of broken stone and sand. The cubes were 1 foot in length of side; the columns were all 12 inches by 10 inches in cross-section, and 3 feet in height. The ferro-concrete columns were of the standard Hennebique construction, having four bars of steel 1¾ inch in diameter placed near

the corners of the pillar and running from top to bottom. At the commencement of the experiments the load was equally distributed on steel and concrete alike, but, owing to the greater compression of the concrete as compared with that of the steel, as the test proceeded the steel carried more and more of the load until the specimen began to fail from the buckling of the bars. This buckling is partly prevented by the lateral tying together of the bars with wrappings of thin round steel placed at frequent intervals. The better results in the case of No. 24 as compared with those of Nos. 22 and 23 are in great measure due to closer spacing of the bindings and more secure fastening to prevent them being pulled open by the buckling of the bars. Where several values are given for the elastic modulus, they refer to the values as calculated from the readings taken during the successive loadings. The curves plotted in Fig. 14 represent the means of the back and front readings taken from the last loading.

Conclusions. The results of the experiments upon the brickwork appear to lead to the following conclusions :—

1. Up to loads considerably in excess of those used in actual practice the strains are sensibly proportional to the stresses.

2. Each of the materials experimented upon possesses a fairly definite elastic modulus, under ordinary loads.

3. With repetition of the load the strain is found to diminish, until, after three or four repetitions, it becomes sensibly constant, possibly owing to the squeezing together of the particles and the closing up of the interstices. This diminution of the strain causes a small increase in the modulus.

4. At loads considerably in excess of working loads, proportionality of strain to stress gradually ceases. The point at which this occurs may reasonably be called the "limit of proportionality."

5. The elastic properties of brickwork, as well as its ultimate strength, appear to depend less upon the bricks than upon the quality of the cementing material.

6. In all cases the best results are obtained where the mortar employed not only provides a highly elastic bed for the bricks, but has the property of adhering to the bricks in their vertical joints, thus knitting the whole into a homogeneous material.

7. It is reasonable to suppose—although the experiments upon this point were hardly complete enough to warrant a hasty generalisation—that the more nearly the elastic coefficient of the mortar approaches that of the bricks, and the more uniform the thickness of the joints, the more uniform will be the stress upon the bricks, and consequently the stronger the brickwork.

8. The diagrams show that with the method employed for setting the specimens in the machine a very uniform distribution of the stress is obtained.

The Electrical Discharge in Air and its commercial application.

By WILLIAM CRAMP and SIDNEY LEETHAM.

IT was in 1903 that Mr. Sidney Leetham discovered, after experimenting with the bleaching of flour by means of ozone, that a much more powerful bleaching agent than ozone was produced if air that had been ozonised were passed through boxes in which electrical discharges between spark points were taking place. It was evident from the smell of the gas that the new product was different from the old, and some time was spent in noticing and attempting to ascertain clearly what this new product was. Dr. H. E. Armstrong made an analysis and about that time wrote : "I am much struck with the nature of the results obtained, viz., the rapidity and certainty with which the effect is produced and the improved bleach as compared with that produced by oxides of nitrogen. I believe . . . . that it is a joint effect of ozone and oxides of nitrogen, which I find are both present, though the total amount is not more than 2 parts in 10,000. I am satisfied that by this mixture an effect is produced which is so far better than anything that can be attained by either of the constituents as to be accounted a *new technical effect.*" From that date to this the authors have been engaged in developing and perfecting a form of apparatus for the production of this gas, and incidentally have touched upon points about the electrical discharge which have not hitherto received attention. For convenience the account of this work is subdivided into four sections—namely : Section I., the construction and application of the apparatus; Section II., the electrical phenomena; Section III., the electrochemical phenomena; Section IV., the chemical phenomena.

SECTION I.

The apparatus as at present used is illustrated in Fig. 1, and consists of a steel plate case, in which is fixed an alternator, transformer, switchboard, ozoniser and sparking device; the whole being compact, self-contained and enclosed, occupies very small space and incurs no extra insurance risk. Besides the apparatus already mentioned, a small Roots' blower is used for supplying air to be ozonised, and a small filter for cleaning this air. The action of the apparatus is as follows :—Pure air cleared from dust particles by passage through the filter is supplied by the blower to the ozoniser (situated behind the switchboard), where it becomes ozonised, and also to some extent sterilised. The ozonised air then passes on to the spark box—seen across the middle of the switchboard—where a very small proportion of oxides of nitrogen appears to be

produced by the sparks between the points in the box. From the spark box the air passes through a valve flange (seen at the left-hand end of the case) straight to the reels through which the product to be bleached is passing. The actual electric circuits are as shown in the diagram of connections (Fig. 2); where the high-tension and low-tension coils of the transformer are denoted by HT and LT respectively; O is the ozoniser of the Andreoli pattern; SB is the spark box, in which are a number of spark gaps in series; AA is the alternator armature and EA is the exciter armature; F_1 and F_2 are the field coils, and R_1 and R_2 the regulating rheostats. It will be noticed that the ozoniser and spark box are in series, and this is a great advantage in rendering the apparatus automatic to a certain extent. For every increase of current affects both ozoniser and sparks, so that within certain limits the proportions of the gas remain constant; though, of course, the yield becomes greater, as more fully discussed later. It may be stated here that with the normal amount of air used, which is approximately 100 cubic feet per minute, the resulting gas, which issues from a point some 3ft. beyond the end of the delivery flange of the iron case, is made up about as follows : Air, 40,000 parts by volume; ozone, three parts by volume; oxides of nitrogen, one part by volume (when four sparks are used, each $\frac{1}{16}$in. long, and the LT current is 8 amperes). This result is the average of a large number of analyses made by Mr. F. S. Sinnatt, of the Manchester School of Technology, and will be seen to agree fairly well with Dr. Armstrong's rough estimate. It will, however, be clearly understood that variations in the above result are immediately introduced by change in any of the following factors :—

1. Frequency.
2. Air stream.
3. Distance apart of spark points and number of these.
4. Shape of points.
5. Temperature.
6. Curreht.

Of these the two last influence the chemical phenomena chiefly. From a scientific point of view the interest lies in the question of how these various items affect not only the gas produced but also the type of discharge which produces it. We shall take the latter point first.

SECTION II.

Hitherto all types of alternating electrical discharges have been divided into three great classes : (1) the ordinary alternating current arc, (2) the high-tension discharge between spark points, (3) the silent discharge. These three have usually been considered as separate and distinct phenomena, but they have never been individually defined. In reality they are not separate, but all stages of

Fig. 1.—Commercial Form of the Electrical Apparatus.

the same phenomenon—namely, the breakdown of air as an insulator when strained electrically. Roughly, the three types have been usually classified by the effect which they produce. In this way the arc has been recognised as that type of discharge which gives great heat and light. The sparking discharge has been
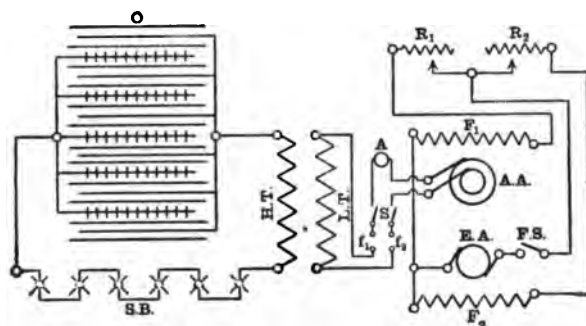
Fig. 2.—Diagram of Connections of the Apparatus shown in Fig. 1.

recognised as that which is much less hot, though still luminous, and is known to produce Hertz vibrations. The silent discharge is usually referred to as that which produces ozone. Now, if a pair of metal points be insulated and separated in air by a small distance, and an electric P.D. be applied across the gap, we have the following series of events as the pressure is increased :—

(a) The air is put into a state of stress.
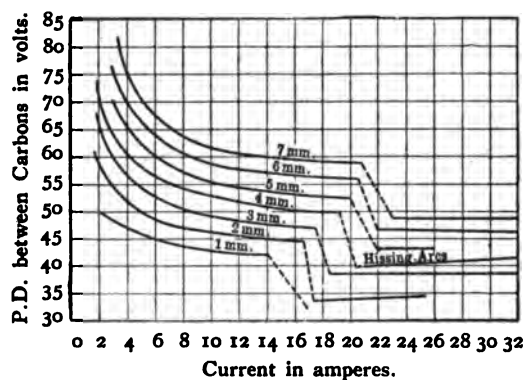
Fig. 3.—P.D. and Current for Different Lengths of Arc (Mrs. Ayrton).
Positive, 11mm. ; Negative, 9mm.

(b) Small conducting paths appear through the air as the resistance gives way, giving rise to small blue streamers issuing from the points.

(c) The blue streamers get thicker, eventually joining the points up.

(d) The thicker streamers become a discharge very like the ordinary arc. At the final stage the points heat up, and the current passing may be gradually increased till the discharge is practically the alternating current arc.

Throughout the changes given above the relation between current and P.D. across the gap is very remarkable. It has been known for a long time that an arc, either direct or alternating current, cannot be maintained on a constant potential circuit unless a steadying resistance or its equivalent is kept in series with it. This has given rise to discussion as to whether a back E.M.F. is present in the arc or not, though it is generally held now that change of air resistance alone is sufficient to account for the peculiarities observed. Whether a back E.M.F. exists or not hardly comes into the province of this paper; but it is perfectly certain that the *apparent* resistance
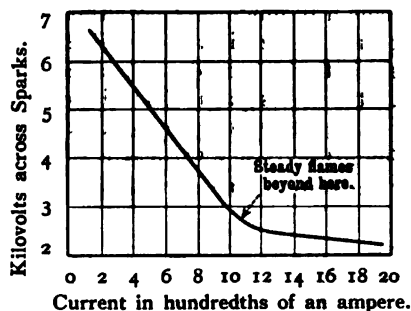
Fig. 4.—Sparks only : Three in Series ¾in.

of the arc changes as the current through it changes. In the case of ordinary arc lights the results immediately met with are generally very like those in Fig. 3, which represents the relationship between P.D. and current in the direct-current arc, as given by Mrs. Ayrton in her book *The Electric Arc*, and reproduced by her special permission. Now, the very same sort of relationship is found to exist with both the other forms of discharge. It will be recognised that the cycle of changes given in *a*, *b*, *c*, *d* above includes not only the spark discharge but also the so-called silent discharge. In Figs. 4 and 5 are shown curves connecting the P.D. and current for cases which include both the silent and the spark discharge. It will be
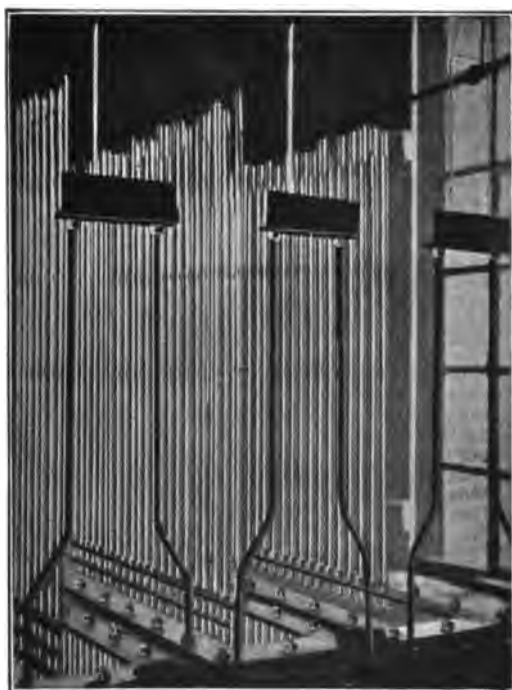
Fig. 6.—Schneller Ozoniser.

seen that just as in the case of the arc the fall of potential is very rapid as the current increases, but finally settles down until it almost becomes proportional to the current.* The diagrams not only show the agreement between the shape of the curves of Figs. 4 and 5 and that given in Fig. 3, which is very important, but also emphasises the fact that it is very difficult to draw any hard and fast lines between the different types of the discharge. It should be explained that as it was desired to act upon air with the various forms of discharge a current of air had to be kept passing through the apparatus. This is why most of the curves above are taken with a certain air velocity, which is given in terms of the blower speed. Thus in Fig. 5, the numbers 420 and 250 refer to the speed of a 2½in. Roots' blower, and correspond to an air stream through the
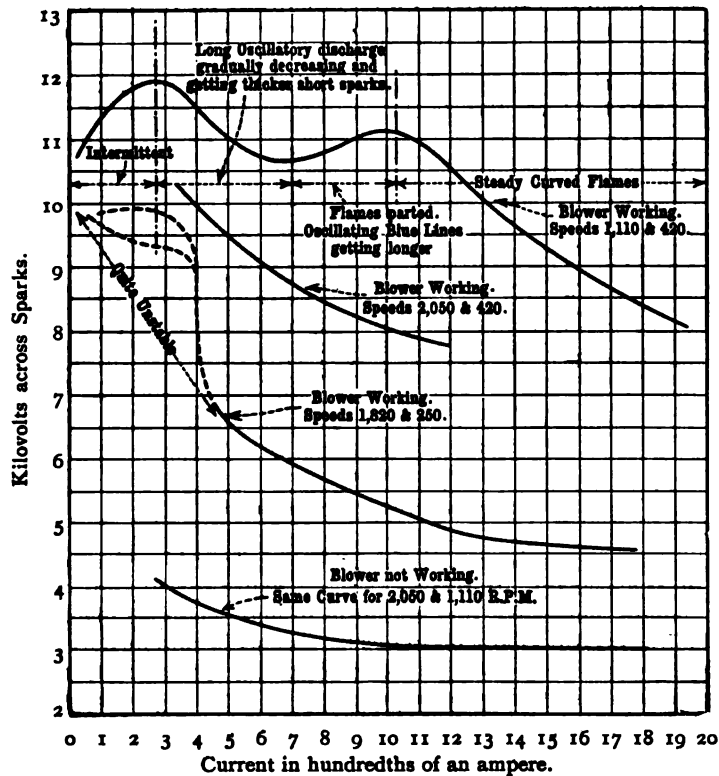
Fig. 5.—Five Sparks, each of ⅟₁₆in. gap.

* In all the curves connecting P.D. and current, where the P.D. is in kilovolts the current is in hundredths of an ampere.

spark box of about 3,200ft. and 1,900ft. per minute respectively.
The effect of this air velocity is (as shown) to increase the P.D. with
a given current; but this will be discussed more fully directly. The
earlier portion of the curves—that is, those parts in which the P.D.
is high—usually refer to that discharge which produces chiefly
ozone. Directly the curve has turned round, so that there is no
longer a large fall in P.D. for a given current, very little ozone is
produced. It is clearly seen from the curves : (1) That the P.D.
across the spark gap gradually decreases as the current increases,
showing clearly that the resistance of all electric discharges varies
in a similar manner to that well known to exist in the case of the
ordinary arc. (2) That the character of the product of the discharge
depends upon the voltage at the terminals for a given current; thus
with the conditions shown in Fig. 4 practically no yield of oxides of
nitrogen occurs until a point is reached marked with an arrow on
the diagram. To the right of this arrow the discharge would be a
small but rather hot arc, were it not for the presence of the air
stream which blows the discharge into a short flame. In other
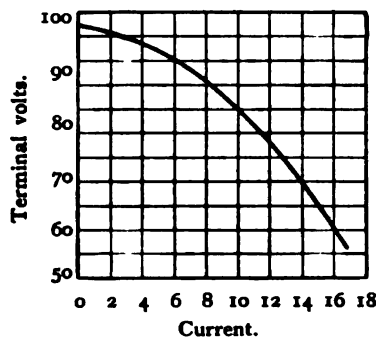
Fig. 7.—Alternator Characteristic.

words, up to this point the discharge is to be considered practically
as a silent discharge, afterwards as the so-called sparking discharge.
The change, however, from one form to another takes place fairly
gradually. (3) Any character of discharge may be obtained by simply
regulating the fall of potential at the discharge points or terminals,
so as to fulfil the following requirements : Since the resistance (or
impedance) of the air gap across which the spark passes appears
to depend not only upon its length but also on the current passing
(being lower with a larger current), it follows that if there were a
constant pressure on the arc, having once started the discharge, the
current would rise till the product $C \times R = E$, where R is the

resistance or impedance of the arc, E the applied P.D. and C the current. If R tends to decrease faster than C rises, the conditions are quite unstable and result in a long series of flashes across the points, which were observed often in the case of these experiments. These flashes are produced by a large rush of current which is only limited by the armature reaction of the generator. In consequence of this, beyond a certain point the E.M.F. and P.D. of the latter fall, so that the current almost instantly falls to zero. As soon as this has happened the E.M.F. rises again, the spark is re-established, another rush of current takes place with a similar result. Often this would take place as frequently as 60 times a minute. To steady the discharge then it is only necessary to arrange the circuit so that an increase of current shall produce at the spark terminals a fall of P.D. sufficiently great, and in this way, by proper adjustment of the circuit, a perfectly steady result will be obtained. The only other conditions necessary for producing and maintaining the discharge are (1) that the maximum P.D. of the E.M.F. wave shall be capable of crossing the spark gap, (2) that the current ensuing shall be great enough to lower the resistance of the gap so that the vapour column set up shall not entirely die away before the zero point is crossed and the current re-established. The adjustment of the circuit just shown to be necessary may be carried out in many ways. In the authors' apparatus it is obtained by the use of a heavy synchronous armature impedance, but it may be almost as well obtained by resistance or choking coils. The higher up the scale the discharge the greater must be the resistance employed; thus, if a silent discharge is required, the resistance drop will need to be from one-third to one-half of the terminal voltage. An instance of such an ozoniser is the well-known Schneller ozoniser shown in Fig. 6, where the potential drop is obtained by means of a tube of glycerine, through which the current passes to those plates, between which the silent discharge takes place. If the ordinary constant potential arc is required, an impedance drop of about one-quarter the terminal voltage is used, while the characteristic of the alternator used by the authors for their purpose is as shown in Fig. 7. The amount of steadying resistance for any type of discharge is affected by :—

1. *The Frequency Employed.* The higher the frequency the less likely is the discharge to be interrupted, and hence the lower is the pressure for a given current. This is well shown in Fig. 5. It is, however, curious that in some cases for very small currents the pressure required is actually raised by raising the frequency. In the apparatus as used by the authors, where the ozoniser and spark box are in series, though, as is shown later, the yield of ozone per ampere may be increased by raising the frequency, yet because the

spark seems to have some difficulty in starting, and because the instability of the circuit does not seem to be reduced by higher frequencies, a practical limit is reached at about 150 to 200 periods per second.

2. *Air Velocity.* The general effect of increased air velocity is to increase the apparent length, and hence, also, the apparent resistance of the spark, and with high air velocities the spark becomes blown out or extended into a flame. The general effects of the air velocity are shown in Fig. 5, and again in Fig. 8. In these diagrams the meaning of the figures 420, 250, 240 has already been referred to. Fig. 5, however, has a second set of figures upon it, viz., 1,110, 2,050, and 1,820. These refer to the alternator

Current in hundredths of an ampere.
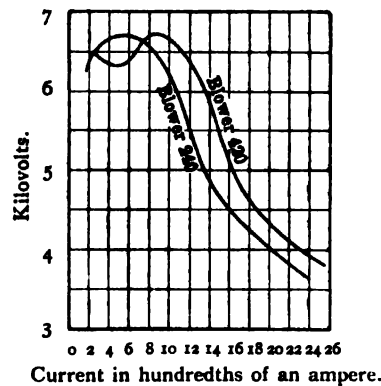
Fig. 8.

speeds, and correspond to frequencies of 148, 273 and 243 respectively. In this way, while Fig. 8 shows the effect of change of air velocity only, Fig. 5 combines with this the effect of change of frequency. The obvious deductions from these curves are that higher frequencies conduce to lower the pressure for a given current, and higher air velocities conduce to higher pressure for the same current. It may be observed that, besides these obvious results, it is also found that a high air velocity sets up very serious oscillations in the circuit, which have many times been responsible for breaking down the high-tension transformers used in these experiments. One would almost expect this result from the fact that the higher the air velocity the more likely is the spark to be very unsteady and very often extinguished. These oscillations show themselves in the curves in giving rise to the unstable portion and causing it to exist at higher currents; and, finally, on account of their disastrous effects it was found necessary to limit the air velocity in the apparatus as at

present used to a maximum of 2,500ft. per minute, with the distance between spark points, say, $\frac{1}{16}$in.

3. *Distance Apart of Spark Points.* Many tests were taken with different spark lengths, as, for instance, five sparks $\frac{1}{16}$in. long in series were compared with four sparks of $\frac{1}{4}$in. long and one of $\frac{1}{16}$in. In the latter case the oscillations in the circuit are found to be greater than with the former, and this general result is true whenever the length of spark is increased. Again, the P.D. with the long spark gaps is always greater than in the case of the shorter, but this effect is not proportional to the number of sparks in series in the apparatus, nor so marked as the increase in oscillations, especially with low currents. So important is the latter that in certain instances
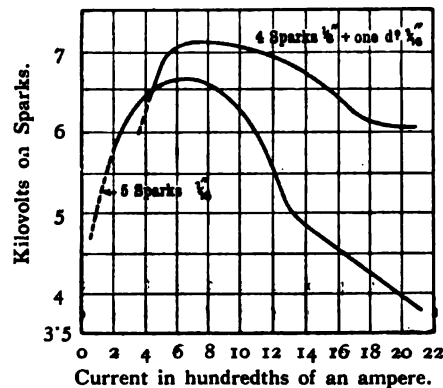
Fig. 9.—Effect of Spark Length (Blower, 240 revs.).

it is not possible to measure the voltage across the sparks at all. It might be expected that the voltage would be almost proportional to the number of sparks in series, but this is not found to be the case at all. On the contrary, Fig. 10 shows that the voltage required for three sparks (each $\frac{1}{16}$in. long) in series, is quite different from that required for one spark $\frac{3}{16}$in. long; further, Fig. 9 shows that four sparks, $\frac{1}{4}$in. long in series, and one of $\frac{1}{16}$in. long, do not take, with small currents, anything like twice the voltage of five sparks $\frac{1}{16}$in. long, as might have been expected. From a great number of experiments the phenomena above detailed seem to be largely explained by the following considerations :—

1. If the spark is a long one the air velocity has more effect upon the discharge, since the points protect it less.

2. Any capacity effect due to the points themselves is more marked when the points are close together.

3 If a vapour column is set up, the longer it is the more easily is it cooled.

These three causes, even taken with others referred to above, do not explain all the effects observed. We must assign to other causes the small increase of pressure for increase of spark length, for instance; also the comparative ease with which the discharges start if no air stream is present (see Fig. 5). The tests given in section 3 upon the question of ionisation will perhaps afford a clue to these points. In the meantime we may mention that the surface leakage over the insulating porcelain has many times been responsible for
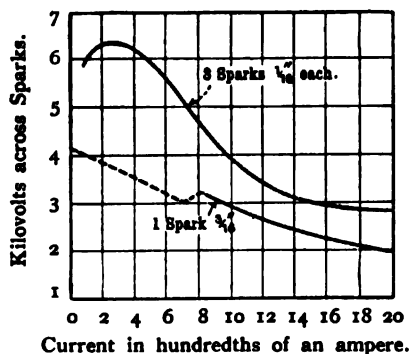
Fig. 10.—Effect of Spark Length : Blower running at 265 revs per min.

starting one spark of a series before the others begin, so that it is usually found that four sparks $\frac{1}{8}$in. in series will start at a much lower voltage than one spark $\frac{1}{2}$in. long. But this fact alone will not explain the phenomenon that to restart the discharge after it has been running for some time requires a much lower pressure than to start the discharge at first; which must also be referred to the state of so-called ionisation in which the gas exists.

Effect of Shape of Points. The shape of the point changes very considerably the apparent resistance of the discharge, and also, in consequence, the type of discharge produced. It is well known, in connection with high-tension discharges, that the sharper the points between which the current passes the lower is the pressure at which the discharge will commence. As an example of this we can give some results obtained at the Manchester School of Technology by Mr. Bertram Scott. In these tests three types of electrodes were used, viz. :—(1) Flat electrodes with rounded edges (in pairs). (2) Flat electrodes with sharp edges and spherical electrodes (one

of each). (3) Sharp or pointed electrodes (in pairs). The results, so far as they influence the pressures used in this apparatus, are as follows :—

1. Flat electrodes with rounded edges.

Kilovolts.	Sparking distance in cm.
18	1·8
29·5	3·9
40	6

2. Flat electrodes with sharp edges and spherical electrodes.

Kilovolts.	Sparking distance in cm.
15	2
24	4
29	5
38	7
46	9

3. Sharp electrodes.

With these it was found that the effect of the sharpness was more marked the less the angle at the apex. The most marked results were obtained with needle points, and it will be noticed that, with such shaped points, the voltage required for a sparking distance of 2 cm. is about half that given in the first case. The figures are as follows :—

Kilovolts.	Distance in cm.
9	2·0
20	4·0
28	6·8
36	9·0
45	10·9

All the above results, of course, would change slightly with change of wave-form; in these cases an alternator was employed whose wave had a form factor of 1·54, so that the shape was approximately sinusoidal. Fig. 10a illustrates these readings graphically. The voltages given are not applicable to the actual apparatus under consideration, since no air current was present except that which would be produced by the actual heat of the discharge; and, since the results were taken when the points were vertical, this would have very little effect. When, however, an air current plays on the discharge, a result similar to the above is always experienced, but the voltage for a given sparking discharge is higher, the actual increase of voltage being of the order of that shown in Fig. 5. It was, therefore, most advantageous for this particular plant, where low voltage is desirable, that the shape of the points should be as sharp as possible. The final shape has been determined by the

question of the life of the spark points—that is, they are so proportioned that they will dissipate the heat generated between them fast enough to necessitate no adjustment of the points, at any rate more often than once a month. The point used now is made from a screw $\frac{1}{2}$in. in diameter, with an apex angle of 90deg., very slightly rounded at the extreme point. It is found that up to 0·2
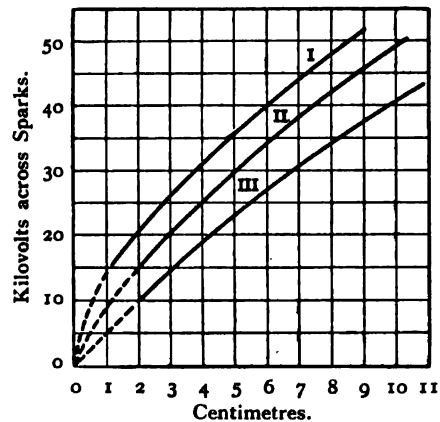
Fig. 10a.—Sparking distance in Air.

ampere, with the normal air velocity as already given, six pairs of these points in a spark box do not materially change when at work night and day for a period of three weeks. The foregoing discussion has been confined chiefly to those portions of the curves where the discharge produced is of the type known as "sparking." It is
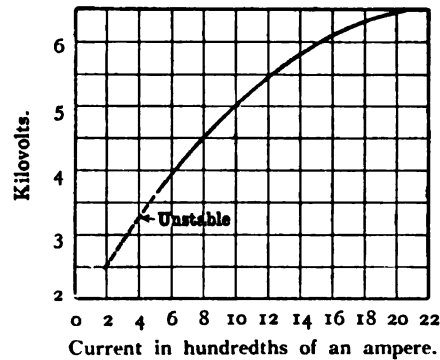
Fig. 11.—Speed 1,200.

necessary now to refer to the upper parts, where, as has been already said, ozone is produced. The figures show quite clearly that in these steep parts the discharge is very unstable, and in consequence a large steadying resistance is necessary, for the current is, in any case, extremely small. This large steadying resistance (or impedance) in commercial ozonisers takes the form of either : (1) A dielectric between the points; (2) very high resistances in series with the points, such as the glycerine tubes of Schneller; (3) a capacity in series with the points. Examples of No. 1 are the ozonisers of Siemens, Andreoli, Elworthy, etc., which usually consist of two conductors, either plain or carrying points separated by mica or glass. In cases like this the fall of potential, which has been shown to be necessary to maintain this silent discharge, takes place across the dielectric itself. Where the points are placed upon sheets, and separated by sheets of mica (Andreoli), the ozoniser may have a large capacity, and in this case the effect of the breakdown of the resistance is very clearly marked. By the laws of condensers, if the ozoniser works as a capacity alone, the current would be proportional to the terminal P.D.; and in this case, therefore, the "curve" connecting voltage and current would be a straight line. If, then, such a curve be drawn for an ozoniser, and it is found to depart from the straight line, we should expect to find the yield of ozone increase as the curve turns over. This effect is clearly shown in Fig. 11, and it was always found that the yield of ozone increased as the curve departed from the straight line, until the vigour of the discharge caused the temperature to rise to such an extent as partially to destroy the ozone produced. Ozonisers of the second type are not as a rule so efficient as the former. They are, however, easy to construct, and, as a rule, less bulky. An ozoniser of this type was constructed by Mr. Cramp, which consisted of a number of serrated strips of aluminium, placed with their serrated edges about $\frac{1}{2}$in. apart. It was found that the minimum air gap between these edges, at which a steady silent discharge, producing large quantities of ozone, could be obtained, was about $\frac{7}{16}$in. and in the experiment in question $\frac{9}{16}$in. actually gave about the best result. In order to steady the discharge a glycerine resistance had to be included in the circuit, of such dimensions that the drop across the resistance was practically equal to the drop across the air gap. By gradually lowering this resistance the discharge could be changed from the silent distributed discharge to the located spark. A large fall of potential was always observed as the discharge changed from one form to the other. Ozonisers of the third form are not made commercially, and the reason is probably that with any tendency of the air gap to break down, the condenser immediately discharges through the circuit, assisting the breakdown; hence the type cannot

be recommended, but it has been found possible to use, in series with the gaps described above, a small condenser which, by the fall of potential which it produced across the gaps, is enabled to a certain extent to steady the silent discharge. Of course, the capacity of the condenser must be of such a value that it cannot (by causing a leading current) raise to any extent the alternator voltage by means of armature reaction.

SUMMARY.

Summarising now the general results of this investigation we have :—

(a) All the types of electrical discharge in air behave similarly, and may be steadied by similar means.

(b) Between a pair of spark points in air any type of discharge may be obtained by suitable regulation—from the silent type producing ozone down to the alternating current arc.

(c) Increasing the number of air gaps in series raises the voltage, but not proportionally to the number of gaps.

(d) An air current, impinging on the electric discharge, increases the mean length of path of the discharge; with large currents, blows it into a flame, renders the spark unable to pass without increased pressure and always sets up oscillations in the circuit.

(e) The effect of increasing the frequency is to lower the voltage required to maintain the spark, but this does not necessarily hold at starting.

SECTION III.—ELECTRO-CHEMICAL EXPERIMENTS.

So many of the results obtained, both electrically and chemically, seemed inexplicable on ordinary grounds, that it was thought advisable to try the gases produced by the electrical discharge for *ionisation*.* Accordingly a series of curves were taken, which show the time required to discharge a good electroscope :—

(a) By allowing the stream of air alone to impinge on the knob of the electroscope.

(b) By substituting for this a stream of air which had passed through the ozoniser.

(c) By substituting a stream of air which had been modified by passing through the spark box.

(d) By combining b and c.

The results are very clearly shown in Fig. 12. They indicate that the air, after having passed through the chambers in which electrification was proceeding, is always in a state of ionisation. This result is much more marked in the case of air issuing from the spark-box than in the case of air which has simply passed through

* The term "ionisation," as used throughout, indicates simply capability of discharging an electroscope

the ozoniser. It is to be considered in connection with the chemical phenomena, but may also be discussed here with reference to the electrical effects.

Suggested Further Theoretical Explanation of Results Obtained. It seemed almost impossible to imagine that these discharges, which require so small a current, could, by any possibility, produce enough heat to set up a vapour column sufficient to maintain a conducting path for the electric current; but, on the other hand, in the absence of the vapour-column theory, there seemed to be no reason why, first, the discharge should be more difficult to start when the air current was flowing, and, secondly, why it should be so much more difficult to maintain with an air current. Admit, however, that ionisation is established and we immediately have an explanation for all the phenomena. Thus, under electrical stress, the air is ionised between the points, and begins to tend to conduct. Small currents make their appearance as blue lines, but whether these blue lines are actually heated particles or not cannot be determined. Further increase of the current results in further ionisation, with a better conducting path; but this conducting path is, under any circumstances, easily removed if a current of air is maintained past and around the points. Thus, the discharge would be more difficult to start and more difficult to maintain. Going still a step further we get towards the ordinary arc, and find that a vapour column is set up, which, of course, continues to behave very much as the ionised air column already suggested. This is, in brief, the theory put forward by the authors to explain the facts already related, and it accords well with previous knowledge of the same subject. Of course, "ionisation" would be immediately admitted by many as sufficient explanation for the whole of the phenomena, and we wish to insist upon the point that without some such theory some of the above facts are inexplicable, especially the point that the discharge starts more easily after it has been at work some time and then extinguished than it does when first set to work. This characteristic is very marked with low air velocities and when the time between stopping and restarting is short. The same may be noticed with a high-tension electrostatic voltmeter. If it flashes over once, the case must be opened and fresh air introduced, or it will go over again at a comparatively low pressure. We think also that this phenomenon will almost certainly account for the extraordinary differences in so-called "sparking-lengths," which have been so often observed and commented upon. Such differences have often been put down to damp and dust, but the authors' experience is that these factors will not altogether account for them. More especially the chemical results, the union of oxygen and nitrogen

particularly, seem impossible without reference to some such theory, as will be seen presently.

SECTION IV.—CHEMICAL PHENOMENA.

It has hitherto been usual to speak of the silent discharge as though it were a perfectly well-known effect, producing a chemical result, well defined. The following experiments will dispel this idea : If an Andreoli ozoniser, such as that whose characteristic is shown in Fig. 11, be connected to alternate-current mains, and the pressure be gradually increased, it is found that a violet glow is set up between grids and mica which produces an excellent yield of ozone; increase of pressure increases the yield of ozone up to a certain point, beyond which the discharge becomes gradually more yellow, and finally quite a large percentage of oxides of nitrogen is produced, the yield of ozone being diminished. Whether ozone is really formed and afterwards destroyed, or actually never formed, is uncertain. Further increase of current still further increases the yield of oxides of nitrogen, though usually by this time long leakage discharges appear over the dielectric. The effects are still more marked if an ozoniser without a dielectric other than air be used, as then the discharge can be gradually increased till practically no ozone is produced; thus the silent discharge becomes the sparking discharge, yielding chiefly N_2O_4; and however much the current be increased after this, even to the flaming arc, the gas produced is still N_2O_4. We have found no type of discharge, however silent, which yields no oxides of nitrogen. We can offer no explanation whatever for the production of ozone by the initial types of discharge. But there are some suggestions we can make as to the formation of oxides of nitrogen. It has been generally assumed that oxides of nitrogen are formed electrically by nitrogen burning in the air, the heat necessary being supplied by the flame of the arc or spark, as pointed out in 1898 by Crookes. Now the temperature of burning nitrogen is supposed to be about 2,000°C.; and though it is impossible to see if this temperature ever exists in the sparking discharge, it seemed almost incredible that such could be the case. In order to try and settle this point recourse was had to the following rough tests :—

Temperature Effect. A spark box with five pairs of points $\frac{1}{16}$ in. apart was placed in circuit and the current adjusted to 0·1 ampere. Tests were then made while the spark box was cold (20°C.) and again when heated to 120°C., but no definite increase in the percentage of oxides of nitrogen was observed. It would therefore seem that the yield is not altogether a matter of temperature. With four $\frac{1}{16}$ in. sparks in series, an air velocity of 2,000 ft. per minute, and a current of 0·06 ampere, the yield of oxides of nitrogen was 1 part in 40,000 as tested by Mr. Sinnatt many times. Again, it is always found that

when air with a small percentage of ozone is passed through the spark box the chief production of oxides of nitrogen does not take place in the spark box, but a little further on, in our case after the gas has passed through about 3ft. of pipe; pipe, too, which is perfectly cool. Or again, if in such a case the small sparks be replaced by white-hot Nernst filaments, no oxides of nitrogen are formed at all. And if further confirmation of the formation being independent of the temperature be needed, we can say that if pure oxygen mixed with 2 per cent. of nitrogen be sent through a water-cooled Berthelot ozoniser, peroxide of nitrogen is still found to be present.

Current. On the other hand, it is always found that the yield of oxides of nitrogen does not increase proportionately to the current, but more slowly. Indeed, in the spark box above referred to there is scarcely any change in the yield of oxides of nitrogen between
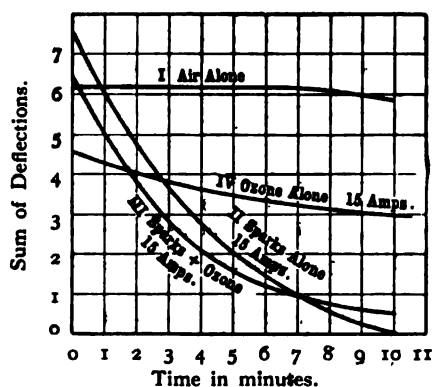
Fig. 12.—Ionisation Experiments.

15 and 25 amperes, which is very remarkable, inasmuch as not only is the current so much greater, but the temperature is also so much higher. On the other hand, between 5 and 10 amperes, the yield is very much increased. The reasons for these effects the authors consider to be as follows :—The best yields per ampere are always found to exist when very thin arcs are used, and this is confirmed by Bradley and Lovejoy, in America. That means, the air used must have easy access to the sparks if a large yield of oxides of nitrogen is desired; this condition accounts for the amount produced not being proportional to the current. Now in Fig. 12 it has been shown that the air modified by a sparking discharge is more highly ionised than that obtained by a silent discharge. Hence we suggest that ionisation of the air allows of the combination of oxygen and nitrogen at fairly

low temperatures to produce oxides of nitrogen, but it is very necessary that the air should be in intimate connection with the discharge to become thoroughly ionised. This theory would seem to be well supported by the fact that replacing the sparks by apparatus which must surely be hotter—such, for instance, as a Nernst filament or a white-hot electric radiator—has no effect at all. With regard to the effects produced on the gas by electrical variations in the circuit, it may be said that a great number of experiments have been carried out, but only the general results can be given here. These are :—Increase of frequency increases the yield of ozone, as shown by Prépognot (Fig. 14), and lowers the pressure for a given current through the spark box. Increase of air velocity does not seem to lower the yield, but only the concentration. Any increase in spark length increases the yield of oxides of nitrogen.
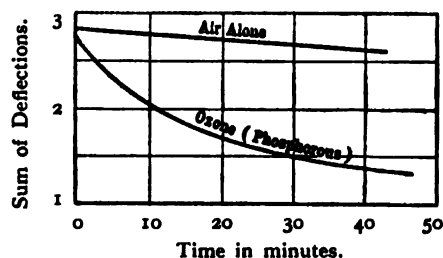
Fig. 13.—Ionisation Experiments.

So much for the independent effects of different types of discharge. We come now to the most important part of the paper, viz., the discovery that, though the gas produced by the sparks (N_2O_4) is valuable as a bleaching and sterilising agent, and the gas produced by the ozoniser (ozone) is valuable in the same way, a combination of the two is far more valuable than either. Reference to the first part of this paper will show the arrangement of the apparatus by which the Leetham gas is produced. It is obtained by passing air modified by an ozoniser through a box in which a sparking discharge is produced. An analysis of the gas produced has already been given, and it only remains to discuss its peculiar characteristics. It has been pointed out as a curious fact that the chief modifications produced by the spark box are not discernible at the end of the spark box itself, but at a point in the pipe situated about 3ft. therefrom. This supports the theory already given for the production of N_2O_4. Beyond this 3ft. or 4ft. the gas analyses show no change, and it is an undoubted fact that, even after the gas has passed through many feet of pipe, ozone and oxides of nitrogen are still

traceable. We regard this as very important, for eminent chemists (Sir James Dewar and others) have stated again and again that such a state of things is impossible—*i.e.*, that oxides of nitrogen and ozone cannot exist side by side. This simultaneous existence of two gases well known to be mutually destructive is probably the key to the whole extraordinary activity of the compound. As an instance of the great effect the gas has, it may be said that modified air, having a composition as shown in section I., will, if supplied at the rate of about 100 cubic feet per minute, bleach to a beautiful white colour as much as 3 tons of flour an hour; a wonderful effect when the proportions of bleaching agents present are considered. In order to try and discover the means whereby this electrical product yields such astonishing effects, very many experiments have been carried out both by the authors and Mr. J. S. Peachey, of the Manchester School of Technology. It is of interest to inquire, firstly, whether

Grammes of Ozone in 70 litres of air.
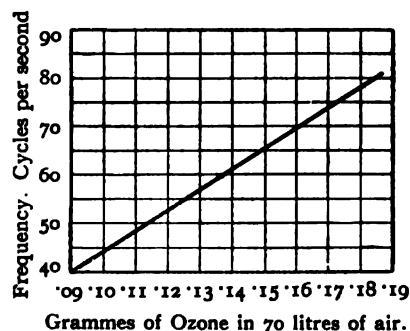
Fig. 14.—Variation in Yield of Ozone, with Frequency.

the bleaching action is due to oxidation. In order to test this, ozone, carefully freed from oxides of nitrogen by thorough washing with pure concentrated sulphuric acid, was allowed to come into contact with flour. *Result: the flour was bleached.* An exactly similar effect was produced if the colouring matter of the flour was separated from the other constituents and treated with pure ozone. Therefore the action may be ascribed to oxidation. Secondly, it is interesting to know whether the ozone and oxides of nitrogen act similarly as bleaching agents. So far this is not quite certain; but it is perfectly certain that the ultimate effect of the two bleachers is different. For ozone, however often applied, never has any other effect than that of bleaching, while oxides of nitrogen only bleach up to a certain point, beyond which they turn the flour darker and darker until it is a sepia colour. The latter effect is probably due to the presence of nitric acid. So far as we have yet discovered oxides of nitrogen and

ozone bleach flour similarly, though the former has other effects besides that of bleaching. Thirdly, we ask why are the two gases when electrically produced so much more powerful than either gas alone. Two theories are possible. (1) That the little proportion of oxides of nitrogen acts as a carrier between the ozone on the one hand and the flour on the other. It may be that by such means ozone is split up more easily, and the authors have certain reasons for inclining to this view. The action is then oxidation, but partially catalytic oxidation. (2) That by passage through the spark box the ozone is rendered much more active because much more highly ionised. Fig. 12 shows how much more ionisation takes place in the spark box than in the ozoniser. It was thought that this question might be settled once and for all by producing the ozone chemically instead of electrically. Pure ozone was, therefore, carefully prepared by Mr. Peachey by means of the well-known action of phosphorus, and this was found to bleach effectively; but on testing with the electroscope it was also found to be in a state of ionisation as shown in Fig. 13, so that the test was quite inconclusive. Work on this subject is still in hand, and the authors can only ask those chemists who have any experience of this kind of work to express their opinions of the possibility of each of the theories above suggested. We may, however, collect, for the benefit of the commercial chemist, the results which have been obtained in this investigation and which will be of use to all those who are seeking to solve the problem of the electrical fixation of nitrogen or the economic production of ozone. The conclusions to which our experiments point are :—

(a) In order to obtain good yields of oxides of nitrogen from the air, it is not essential that a very high temperature should be used. Very thin electric discharges existing between many pairs of points (the latter being as far apart as insulation will allow and supplied by alternating current of high frequency) will give, probably, the most economical results. By this means long flames of burning nitrogen may be producedwhich do not appear to have a temperature approaching that of the arc, but yield, nevertheless, as much oxides of nitrogen with a smaller expenditure of power. Good results are to be looked for, not by increasing the current supplying those points so much as by increasing the number of pairs of points used. The use of a current of air to extend these discharges is certainly to be advocated, but the limit of the velocity of this air current is determined by the oscillations set up in the circuit thereby; for above a certain point no commercial insulator will stand the effect of these latter. The points used should be conical in shape, of such proportions that they do not readily burn away. Steel is, perhaps, the best material.

(b) In order to obtain good yields of ozone electric discharges should be allowed to take place between edges or points, these discharges being controlled by a high steadying resistance or impedance so that they cannot possibly develop into that form of discharge which is so concentrated that it may be blown into a flame. An alternating current of high frequency should be used, and to avoid the production of oxides of nitrogen, the air supplied should be dry, clean and cold, and every precaution should be taken to keep the whole apparatus cool, as, with high temperature, ozone is immediately split up. The current may be increased so long as no yellow discharges appear, and no sensible heating of the apparatus takes place. In order to make the apparatus as economical as possible, the air gap used should be long, for then the loss in the steadying resistance is proportionately less, but the over-all pressure is proportionately higher. The authors consider that the observance of the above conditions will materially tend to economy in the commercial application of the electric discharge.

Biological Tests. A number of tests have been made to prove the sterilising effect of the gas, and the following are the chief results, as given by Dr. F. M. Blumenthal. The quantity of micro-organisms in 1 gramme was :

Bleached rye meal.	Unbleached rye meal.	Bleached wheat flour.	Unbleached wheat flour.
1,600	2,400	170	540

The flour is thus seen to be partially sterilised, and this fact is found to increase very materially the value of the process, since it improves so much the keeping properties of the material treated.

Influence of Certain Reagents

on the tensile strength and on the
dyeing properties of cotton yarn.

By Mr. JULIUS HÜBNER and Prof. W. J. POPE, F.R.S.

ALTHOUGH an exact knowledge of the changes in the tensile strength of cotton yarn which result from treating the latter with various reagents would undoubtedly be of great importance in connection with the textile industries, very little has as yet been done towards obtaining such knowledge; further, the information which is available upon this subject is practically entirely of a qualitative nature, and few results of a really quantitative character have been published, even on so old and important a technical process as that of mercerisation. In view of the lack of data capable of guiding investigation upon the subject, we have thought it desirable to make a preliminary study more particularly of the way in which the tensile strength of a raw cotton yarn is affected by treatment with solutions of a number of inorganic salts and with caustic soda solution in order to ascertain in which direction we may most profitably push a more extended inquiry we have in contemplation. For the purpose of obtaining a measure of the strength of yarn for practical purposes, it seems to be the most generally adopted practice to stretch a lea of the yarn between two steel hooks or arms, and then to ascertain the weight required to draw the arms apart and break the lea. This method is, however, open to the objection that it must be practically impossible so to spread the lea out between the two arms as to ensure an equal distribution of the strain amongst all the threads; some of the latter will necessarily receive more of the pull than others, and, since the lea will then be gradually torn, owing to some threads breaking before others, the breaking load registered will be less than the sum of the breaking loads of the individual threads. As it was desirable to have experimental data, obtained with a machine of this type, for comparison with the results given by the method we ultimately adopted for ascertaining the tensile strength of yarns, Mr. W. Myers, of this School, kindly reeled a portion of the raw Egyptian yarn described below into leas, which were then broken in a Nesbitt tearing machine; the counts and the breaking loads of the 18 leas thus prepared are given in Table I. It will be seen that the breaking load varies from 77·0 to 111·9 lbs., which, when reduced to a basis of 100 for the convenience of future comparison, indicates a variation of from 100 to 145·2; the mean breaking load is 99·0 lbs., and as the tension is borne by 160 threads, each thread carries an average of 277·9 grms. at the breaking load. The lea does not, however, break as a whole, but, as the load is increased, individual threads break

one after the other, until so many have broken that the remainder slip and the arms of the machine move easily apart; the number 277·9 grms. cannot therefore be regarded as the mean breaking load of a single thread, and, as we show in Table II., it is far below the true mean tensile strength of a single thread. The uncertainty which exists as to the proper interpretation to be given to the numerical

Table I.

Hanks to the pound.	Breaking Load in pounds.	Hanks to the pound.	Breaking Load in pounds.	Hanks to the pound.	Breaking Load in pounds.
26·3	90·2	26·3	90·2	26·0	109·4
26·0	92·8	26·0	105·2	25·6	111·9
26·7	90·5	26·0	77·5	26·0	108·1
26·3	83·5	26·0	100·0	26·3	102·2
26·3	96·0	26·3	105·3	26·0	106·9
26·7	87·0.	26·3	109·4	27·0	98·4

values obtained by this method is intensified by the machine being driven by hand and therefore not at a constant speed. Dividing the numbers given in Table I. into a first and second set of nine each, the first nine give a mean of 90·3 lbs., and the second nine a mean of 105·7 lbs., as the breaking load; the great increase in the mean is due to the natural tendency to work the machine more rapidly as the observations accumulate. As no definite meaning could be attached to the results obtained with this machine we discontinued its use. For the tests described in the following pages we used the tearing machine made by Louis Schopper and described by Dalén (Mitt. k. tech. Versuchsanstalt, 1901), in which a single thread, loaded with a weight of 2 grms. in order to keep it straight, is held between clips fixed at a definite distance apart, and in which, by a simple hydraulic device to ensure the load being increased at a uniform speed, the clips are pulled apart gradually, and without any sudden jerk. The load under which the thread snaps is indicated on one scale, and the extension at the moment of breaking is shown on a second scale. The machine which we have used carries a maximum load of 1 kilo. and reads to 5 grms. Although those who have previously published upon the influence of chemical treatment on the tensile strength of yarn have, as a rule, been content to determine the breaking strength of the yarn as the mean of ten or a dozen tearing trials, it seemed to us very improbable that a mean result of satisfactory accuracy could be obtained by such a method of working. Cotton yarn being a product obtained by twisting together a number of fibres of different lengths and thicknesses by a mechanical process incapable of insuring absolute uniformity of count and twist, it seemed likely that the recorded breaking strains of individual threads of the most uniformly spun yarn obtainable would differ so considerably that perhaps 100 threads would have

to be broken before data capable of yielding the mean tensile strength of the yarn with any degree of accuracy could be obtained. This preliminary view of the nature and number of the determinations to be made led us to lay in a considerable stock of the most uniformly spun raw twofold 50 Egyptian yarn which we could select. A lea was then reeled off from the raw yarn, cut across into short threads, each of which was then broken in the tearing machine, the tensile strength and the extension at the breaking load being noted. The results obtained are given in Table II., in which column 2 states the number of threads breaking at the load indicated in column 1. An inspection of this table shows that the 99 threads from the same lea varied in breaking stress from 330 to 440 grms. (or from 100 to 133·3), and conclusively proves the correctness of our view that no accurate mean value for this constant can be derived from the examination of a few threads. The mean breaking strength of the

TABLE II.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
330	2	370	11	410	6
335	2	375	1	415	2
340	2	380	5	420	2
345	3	385	9	425	1
350	5	390	5	430	2
355	7	395	6	435	1
360	12	400	5	440	1
365	6	405	3		

Mean tensile strength, 378·0 ± 1·7 grms. Number of observations, 99. Length broken, 10 cm. Limits of observed breaking loads, 330 and 440 grms. Ratio of same, 100 to 133·3.

raw yarn, deduced from the table is 378·0 grms., and since it is necessary to obtain some knowledge of the extent to which this mean result can be relied upon, we apply to the determinations the method of least squares; taking the number of determinations as n, the n observed breaking strains as S_1, S_2, S_3, ...S_n, and the mean breaking strain as M, the deviations Δ_1, Δ_2, ...Δ_n, of the individual determinations from the mean value, are $M - S_1$, $M - S_2$, ...$M - S_n$, and in the equation—

$$r = \pm 0·6745 \sqrt{\frac{\text{Sum of the } \Delta^2}{n\,(n-1)}}$$

the value r represents the probable error of the mean value. Since, in Table II., $r = \pm 1·7$ grms., it follows that it is just as likely that the true mean value of the breaking strength of the yarn lies between the values 376.3 and 379·7 grms., as that it lies outside these limits; the mean value deduced from the above 99 determinations is therefore probably accurate to within 0·45 per cent.

In applying the method of least squares as a criterion of the accuracy of the mean tensile strength ultimately calculated, it should be pointed out that, in the present set of tests, all the conditions requisite to the legitimate application of the mathematical method are not fulfilled. Thus it will be noted that the greatest frequency with which a particular breaking load is observed amongst any one set of our determinations is not, as a rule, that nearest to the mean tensile strength, whilst the curve obtained by plotting the recurrence of the particular breaking loads against the breaking load is not a curve showing only one maximum. In Table II. the breaking load 360 is observed the greatest number of times, viz., 12, whilst breaking loads 375 and 380, those nearest the mean of 378·0, only occur once and five times respectively; further, the curve shows the

Breaking Load in Grams.
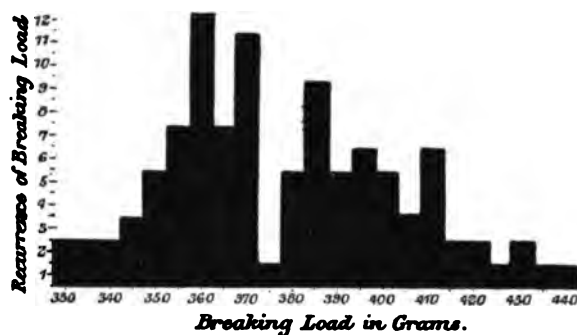
existence of several maximum values, more particularly at the loads 360, 370, and 385. These and other peculiarities to be noted in the tables—as for instance the occurrence of the load 370 eleven times and of 375 only once—might be attributed to faults in the machine, such as a tendency to register 370 more readily than 375; We have, however, proved that the machine possesses no such bias, by adding up from all the tables the frequencies with which different breaking loads recur. After arguments such as the foregoing against the application of the method of least squares have been considered, it must still be agreed that the method constitutes a perfectly reliable one for obtaining a comparative measure of the degree of accuracy attained by such series of tests as those now put forward. It should be pointed out that experimental determinations of a constant are of no value for comparative purposes unless the probable degree of accuracy of the measurement can be stated; the mean values of the tensile strengths of yarn treated in various ways deduced from 10 or a dozen observations, and accompanied by no discussion of their probable accuracy, hence have very little bearing on the

problems they are intended to elucidate. Having now obtained a satisfactory method of determining the mean tensile strength of a cotton yarn within very narrow limits of error, and knowing that Egyptian yarn is only with difficulty wetted out, the main stock of the raw yarn was boiled for two hours in water, left in steep for two days, boiled for one hour in a 1 per cent. sodium carbonate solution, and washed in distilled water until free from soda; the yarn was not treated with caustic soda for the purpose of cleaning it, as it was desirable as far as possible to avoid any chemical action upon the yarn. After the yarn had been air-dried, Professor T. W. Fox, of this School, was good enough to have it reeled into leas of 120 threads, one of which was used in each of the determinations described below. Table III. refers to the examination of a lea of this material (which we may conveniently name A) after it had been scalded in boiling water for two minutes and dried one day in the air. It should be stated that all the tearing trials recorded in the present paper were made whilst the hygrometer indicated 55 to 65, and after the yarn had been exposed for at least 24 hours to the air.

TABLE III.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
285	1	390	3	440	3
335	1	395	6	445	5
350	1	400	11	450	7
355	1	405	6	455	7
360	1	410	3	460	5
365	1	415	11	465	4
370	3	420	11	470	1
375	3	425	5	475	1
380	5	430	6	480	1
385	3	435	2	510	1

Mean tensile strength, $417 \cdot 4 \pm 2 \cdot 1$ grms. Number of observations, 119. Length broken, 10 cm. Limits of observed breaking loads, 285 and 510 grms. Ratio of same, 100 to 179.

It will be seen that the tensile strength of the yarn has been increased by this cleansing treatment to $417 \cdot 4 \pm 2 \cdot 1$ grms., and from the magnitudes of the probable errors to which the sets II. and III. are liable, it cannot be doubted that we are justified in concluding that during the boiling and steeping in water, and the boiling in a 1 per cent. sodium carbonate solution, the tensile strength of a raw cotton yarn increases considerably. This increase in strength would seem to be attributable to the boiling in water, and not to the action of the sodium carbonate, which only serves the purpose of removing greasy matters; this is indicated by a third set of determinations (Table IV.) made upon a lea of the material A after it had been scalded, left for six days in a 15 per cent. sodium carbonate solution, and washed and dried.

The mean tensile strength, $419\cdot7 \pm 2\cdot2$ grms., is numerically identical with that deduced from Table III., viz., $417\cdot4 \pm 2\cdot1$ grms., and it therefore seems that a 15 per cent. solution of sodium carbonate has no more action on the tensile strength of the yarn than a 1 per cent. solution. No satisfactory explanation, based on experimentally determined facts, has yet been offered for the considerable changes in the tensile strength of cotton yarn which

TABLE IV.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
325	1	390	2	445	6
330	1	395	9	450	6
340	1	400	5	455	6
345	2	405	4	460	1
350	2	410	10	465	3
360	1	415	3	470	4
365	1	420	5	475	4
370	1	425	7	490	1
375	3	430	8	495	1
380	3	435	5	505	1
385	5	440	6		

Mean tensile strength, $419\cdot7 \pm 2\cdot2$ grms. Number of observations, 118. Length broken, 10 cm. Limits of observed breaking loads, 325 and 505 grms. Ratio of same, 100 to $155\cdot4$.

result from chemical treatment of the yarn; further, no quantitative explanation of the variation in tensile strength of different threads from the same lea of yarn has yet been given. Now, however, that we have determinations of the tensile strength of yarn, possessing a known and high degree of accuracy, we are able to put forward tentatively conclusions concerning the points mentioned, reserving for a later date a more complete experimental study of the conditions than is possible in this preliminary paper. A little consideration will show that the tensile strength of a yarn which contains n fibres in the cross section is but remotely connected with the tensile strength of the n individual fibres, for, on breaking a thread by the application of a certain load, the mean effect of the load is to pull the fibres apart, a much smaller number than n being broken, and being broken at different times. So long as the tensile strength of the yarn is less than n times the tensile strength of a single fibre, the strength of the fibres is of quite subordinate importance, and the main factor determining the strength of the yarn is the closeness of the twist, and, perhaps also, a specific adhesion or "cling" exerted between the fibres; it would be expected, therefore, that variations in the twist would show themselves in variations in the tensile strength of the yarn. Mr. W. Myers kindly made a series of 58 determinations of the twist on 10-in. lengths of the raw Egyptian yarn used in the present work, from which it appears that the twist varies from $22\cdot0$

to 30·3 turns per inch, the mean being 25·66 turns per inch. The twist being the main factor in determining the tensile strength of a cotton yarn, it is interesting to notice that the above three figures relating to the twist of the yarn, viz., 22·0, 30·3, and 25·66 are in the ratio 324 : 446 : 378, which is practically the same as the ratio 330 : 440 : 378, of the lowest, highest, and mean values of the tensile strength taken from Table II. This would indicate that for one and the same yarn the tensile strength is directly proportional to the twist. On making a count of the fibres in the yarn with which we have worked it was found to contain an average of 100 fibres in the cross section. If the above reasoning is correct, each fibre of the raw yarn has a tensile strength greater than 387/100, or 3·87 grms.; and further, if a series of tests be made under conditions which interpose a resistance to the drawing apart of the fibres, and which increase the number of fibres which have to be broken before the yarn breaks, a great increase in the tensile strength of the yarn should be observed. These conditions would be attained by making the length of thread to be broken less than the average staple of the yarn. Table V. gives determinations of the tensile strength of the raw yarn made by diminishing the distance between the clips in the tearing machine to 1 mm., so that the yarn is broken in lengths of 1 mm. instead of 100 mm. as in the trials given in Table II.

TABLE V.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
360	1	440	2	510	2
365	1	445	6	515	4
370	1	450	1	520	4
380	1	455	4	525	5
385	1	460	1	530	2
390	1	465	5	535	2
400	3	470	6	540	3
405	1	475	2	545	4
410	1	480	1	550	2
415	2	485	7	555	2
420	1	490	3	565	5
425	5	495	5	575	1
430	1	500	1	590	1
435	7	505	2		

Mean tensile strength, 479·4 ± 3·4 grms. Number of observations, 110. Limits of observed breaking loads, 360 and 590 grms. Ratio of same, 100 to 163·9.

The tensile strength determined on a length of 1 mm. is 479·4 ± 3·4 grms., whilst that made on a length of 100 mm. is 378·0 ± 1·7 grms., so that, as was to be anticipated, the very short length gives a very much higher tensile strength. Determinations of the tensile strength of single fibres, as also an investigation of the relation between the length of thread·broken and the mean tensile strength, are now in progress.

In order to study the influence of mercerisation upon the tensile strength of yarn, leas of material A were scalded for two minutes in boiling water and left for 24 hours in caustic soda solution of sp. gr. 1·342; after exhaustively washing and drying in the air, the tensile strength was ascertained as before, with the results given in Table VI. A parallel trial was also carried out, in which the lea was left for six days in the caustic soda solution, with the results stated in Table VII., for the purpose of ascertaining whether the action of the soda is greater in six days than in one.

TABLE VI.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
355	2	505	6	580	2
400	1	510	7	585	3
405	1	515	3	595	8
410	1	520	1	600	3
425	1	525	4	605	1
435	2	530	1	610	2
440	2	535	7	615	2
445	1	540	2	625	1
450	1	545	4	630	1
460	2	550	2	635	1
470	2	555	5	650	1
475	5	560	1	655	1
485	4	565	3	665	1
490	3	570	5		
495	7	575	5		

Mean tensile strength, 530·9 ± 3·8 grms. Number of observations, 118. Length broken, 5 cm. Limits of observed breaking loads, 355 and 665 grms. Ratio of same, 100 to 187·3.

TABLE VII.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
400	1	500	2	585	2
415	1	505	7	590	1
420	1	510	3	595	2
425	1	515	3	600	1
430	1	520	3	605	3
435	2	525	3	610	2
440	5	530	6	615	3
450	1	535	2	625	2
455	3	540	3	630	1
460	2	545	4	640	1
465	2	550	1	645	2
470	3	555	3	660	1
475	5	560	2	665	1
480	5	565	5	670	1
485	2	570	1	675	1
490	5	575	1		
495	4	580	3		

Mean tensile strength, 526·3 ± 3·8 grms. Number of observations, 120. Length broken, 5 cm. Limits of observed breaking loads, 400 and 675 grms. Ratio of same, 100 to 168·8.

Since the mean tensile strengths, 530·9 ± 3·8 grms. (1·342 NaHO for 24 hours) and 526·3 ± 3·8 grms. (1·342 NaHO for six days), are numerically equal, it has to be concluded that if 1·342 caustic soda has any effect on the yarn after one day's action, that effect is but small and involves an alteration in the tensile strength of less than 1 per cent. Since it is important that further experimental evidence should be obtained in justification of the application of the method of least squares as a means of ascertaining the degree of accuracy to which the mean tensile strength of yarn had been determined, we made a second series of experiments similar to those summarised in Table VII., immersing a new lea of the yarn A in fresh 1·342 caustic soda, at a subsequent date, for six days. The results are given in Table VIII.

TABLE VIII.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
355	1	490	3	565	5
375	1	495	1	570	4
395	1	500	3	575	3
400	1	505	8	580	3
430	1	510	1	585	4
435	1	515	6	590	1
440	2	520	6	595	3
445	2	525	1	600	2
455	2	530	3	615	1
460	3	535	10	620	3
465	2	540	2	635	1
470	5	545	8	660	1
475	3	550	2	700	1
480	3	555	1		
485	3	560	1		

Mean tensile strength, 523·9 ± 3·5 grms. Number of observations, 119. Length broken, 5 cm. Limits of observed breaking loads, 355 and 700 grms. Ratio of same, 100 to 197·2.

The fact that the mean tensile strengths, 526·3 ± 3·8 grms. (Table VII.) and 523·9 ± 3·1 grms. (Table VIII.), are numerically identical, affords further confirmation of the legitimacy of our method of dealing with the experimental results. The action of cencentrated caustic soda upon yarn constitutes practically the only mild chemical action upon cotton to which attention has been directed; we have observed, however, that potassium iodide has superficially much the same effect upon cotton as has caustic soda. On pouring saturated potassium iodide solution upon reeled yarn the hank "wets out" immediately, just as with caustic soda, the fibres becoming at once transparent and assuming a glassy appearance; this rapid penetration of the solution is accompanied by appreciable shrinkage. After washing the yarn several times with absolute alcohol and drying, it retains about 15 per cent. of potassium iodide; yarn thus impregnated

soon turns brown on exposure to air and light, but only colours slowly if sealed up in a glass tube with air and exposed to light. No discolouration occurs on exposing the impregnated yarn to sunlight in a vacuum. By treatment with water the potassium iodide may be rapidly washed out. Further, on agitating filter paper with potassium iodide solution it rapidly disintegrates and forms a pulp just as if caustic soda is used. In view of the great similarity of action of caustic soda and potassium iodide upon cellulose it seemed desirable to attempt to isolate a compound of cellulose and potassium iodide analogous to the compound of cellulose and caustic soda which Gladstone (*Journ. Chem. Soc.*, 1852, 5, 17) obtained by washing mercerised cotton with absolute alcohol until the washings contained no more soda; we found, however, that absolute alcohol slowly but completely extracted all the potassium iodide from a hank of cotton yarn which had been soaked in saturated potassium iodide solution for 24 hours. This fact indicates that the combination between cellulose and potassium iodide is of a less stable character than that between cellulose and the caustic alkali, because Gladstone found (*loc. cit.*) that the compound of potash and cellulose is not decomposed by absolute alcohol, although the latter solvent dissolves caustic potash. The similarity between mercerisation and treatment with potassium iodide solution is intensified by our observation that cotton yarn which has been soaked in saturated potassium iodide solution for 24 hours and washed in distilled water until free from iodine, has a far greater affinity for direct cotton colours, such as benzopurpurin 4 B, than has the untreated yarn; it is also to be noted that, after treatment with potassium iodide solution and washing, the yarn burns in the peculiar way which Gladstone first called attention to in connection with mercerised cotton. A further similarity between the action of caustic soda and potassium iodide upon cotton is found in that both reactions result in an increase of the

TABLE IX.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
305	1	410	3	465	2
340	1	415	5	470	6
350	1	420	4	475	2
365	1	425	6	480	1
375	1	430	9	485	2
380	4	435	8	490	2
385	4	440	7	495	2
390	6	445	6	500	1
395	1	450	7	505	3
400	5	455	4	520	1
405	7	460	5		

Mean tensile strength, 431·6 ± 3·8 grms. Number of observations, 118. Length broken, 10cm. Limits of observed breaking loads, 305 and 520 grms. Ratio of same, 100 to 170·5.

tensile strength of the yarn. Table IX. gives the results of a trial made upon material A after scalding for two minutes, immersing for 24 hours in saturated potassium iodide solution, washing until free from iodine in distilled water and drying in the air. Table X. states the result of an otherwise similar trial, in which the yarn remained for six days in the saturated iodide solution.

The tensile strength of the original yarn, viz., 417.4 ± 2.1 grms., is increased to 431.6 ± 2.3 grms. by 24 hours' immersion in saturated potassium iodide and to 420.4 ± 2.1 grms. when the immersion is prolonged for six days; it is therefore not to be doubted that a considerable increase in tensile strength results from 24 hours' action of the potassium iodide solution, whilst six days' action causes the higher tensile strength to diminish to practically the original value, 417.4 ± 2.1 grms., being numerically identical with 420.4 ± 2.3 grms. If potassium iodide be left in the hank, rapid tendering ensues and a brown colour is developed on exposure to the air, but the diminution in tensile strength after six days' treatment is not attributable to the liberation of iodine, as the solution, which was kept in the dark, remained colourless.

TABLE X.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
315	1	395	2	450	4
330	2	400	7	455	1
345	1	405	7	460	8
350	1	410	8	470	2
355	1	415	19	475	2
365	1	420	8	480	3
370	1	425	8	490	1
375	2	430	7	495	1
380	3	435	3	500	1
385	1	440	3		
390	3	445	6		

Mean tensile strength, 420.4 ± 2.1 grms. Number of observations, 118. Length broken, 10 cm. Limits of observed breaking loads, 315 and 500 grms. Ratio of same, 100 to 158·7.

For the purpose of determining whether the action of potassium iodide is a specific one, or whether it can be caused by solutions of other soluble iodides, we repeated the above experiments, using solutions of barium iodide, potassium mercuric iodide, and barium mercuric iodide. A hank of the material A, after scalding for two minutes in boiling water, was immersed for 24 hours in a saturated aqueous solution of barium iodide, and, after washing till free from barium and iodine, was allowed to dry in the air; the results obtained on determining its tensile strength are given in Table XI. The table indicates that treatment with barium iodide solution causes an

increase in the tensile strength of the yarn from 417.4 ± 2.1 to 433.4 ± 3.0 grms. On immersing cotton yarn in a saturated aqueous solution of potassium mercuric iodide, it wets out instantaneously and assumes the gelatinous appearance presented by the yarn on treatment with caustic soda. On washing with a large bulk of water mercuric iodide is precipitated in the fibres, but slowly dissolves when the hank is left in contact with the washing liquor. This

TABLE XI.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
310	1	395	4	460	4
315	1	400	7	470	6
320	1	410	10	475	2
335	1	415	3	480	4
340	1	420	4	485	3
350	1	425	4	490	3
360	1	430	4	495	3
370	2	435	2	500	1
375	1	440	8	510	2
380	4	445	7	530	2
385	5	450	7	555	1
390	3	455	4	570	2

Mean tensile strength, 433.4 ± 3.0 grms. Number of observations, 119. Length broken, 5 cm. Limits of observed breaking loads, 310 and 570 grms. Ratio of same, 100 to 183.9.

indicates that both potassium and mercuric iodide combine with the cellulose, but that the potassium iodide compound is dissociated, on the subsequent addition of water, more rapidly than the mercuric iodide compound; mercuric iodide being subsequently liberated by the dissociating action of the water, and being insoluble in water, does not dissolve unless left in contact with the washing water containing potassium iodide. If, however, the two iodides were retained by the fibre by capillary action, the same behaviour might be anticipated, as Trevor has shown (Zeits. f. phys. Chem., 7, 468), that that constituent of a double salt which has the higher molecular weight diffuses the more slowly. On treating the yarn with potassium mercuric iodide solution, and subsequently washing till free from iodides, it is found to have an increased affinity for benzopurpurin 4 B; further, on passing the solution of the double iodide through a filter paper, the latter swells greatly and becomes gelatinous, and on shaking filter paper in a test tube with potassium mercuric iodide solution a pulp is formed, owing to disintegration of the paper. The numbers given in Table XII. were obtained with a lea of material A, scalded for two minutes in boiling water, immersed for 24 hours in a saturated potassium mercuric iodide solution, washed until free from iodine and mercury, and dried in the air; Table XIII. shows the result of a similar course of treatment, but in

which the hank was left immersed for six days in the iodide solution. During the action of the double iodides the yarn shrinks very considerably.

TABLE XII.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
330	2	420	3	485	1
350	2	425	2	495	1
360	1	430	6	500	1
370	1	435	5	510	2
375	1	440	5	520	2
380	2	445	4	525	1
385	1	450	7	530	2
390	5	455	11	535	1
395	2	460	6	545	1
400	6	465	2	550	2
405	1	470	5	570	1
410	3	475	5	590	1
415	8	480	7		

Mean tensile strength, 444·9 ± 2·9 grms. Number of observations 119. Length broken, 5 cm. Limits of observed breaking loads 330 and 590 grms. Ratio of same, 100 to 178·8.

An inspection of Tables VIII. and IX. and XII. and XIII. shows that the increase in the tensile strength of cotton yarn due to the action of potassium mercuric iodide is much greater than that caused by potassium iodide alone, although the effect of both these reagents is much less than that of caustic soda. On immersing leas of the material A in saturated aqueous barium mercuric iodide the same rapid "wetting out," and the same parchment-like appearance are noted, but after washing the leas free from iodide they are found to have shrunk much more than when the other iodides are used. Tables XIV. and XV. give results of tests made upon leas of

TABLE XIII.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
325	1	425	7	490	2
355	1	430	4	495	1
365	1	435	2	500	2
375	2	440	7	505	2
380	2	445	2	510	2
385	3	450	7	515	2
390	3	455	2	520	1
395	2	460	10	525	2
400	8	465	5	530	1
405	3	470	3	540	1
410	5	475	7	575	1
415	6	480	2		
420	3	485	3		

Mean tensile strength, 443·4 ± 2·7 grms. Number of observations, 118. Length broken, 5 cm. Limits of observed breaking loads, 325 and 575 grms. Ratio of same, 100 to 176·9.

material A, scalded for two minutes in boiling water, immersed for one and six days respectively in a saturated aqueous solution of barium mercuric iodide, and subsequently washed free from iodides and air dried. It is evident that the action of barium mercuric iodide solution in increasing the tensile strength of the yarn is as great as that of caustic soda, and further, just as with other iodides, the

TABLE XIV.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
395	1	495	3	575	1
405	1	500	2	580	2
420	1	505	2	585	1
425	2	510	3	590	1
440	1	515	5	595	3
445	1	520	9	600	5
450	1	525	1	605	2
455	1	530	5	610	2
460	1	535	3	615	1
465	1	540	4	620	2
470	1	545	6	625	1
475	3	550	2	640	3
480	4	555	4	650	2
485	2	560	1	670	1
490	3	565	2		

Mean tensile strength, 534·3 ± 3·9 grms. Number of observations, 103. Length broken, 5 cm. Limits of observed breaking loads, 395 and 670 grms. Ratio of same, 100 to 169·6.

TABLE XV.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
425	1	500	3	565	3
430	2	505	4	570	2
440	1	510	3	575	2
445	4	515	3	580	3
450	3	520	7	585	4
455	1	525	3	590	1
460	4	530	5	595	4
465	3	535	8	610	1
470	3	540	6	620	1
475	5	545	5	635	2
480	1	550	5	640	1
490	2	555	3	650	1
495	3	560	3	715	1

Mean tensile strength, 526·6 ± 3·3 grms. Number of observations, 117. Length broken, 5 cm. Limits of observed breaking loads, 425 and 715 grms. Ratio of same, 100 to 168·2.

increase in tensile strength is less after six days' action than after one day. It has also to be noted that cotton yarn dyes much more strongly with benzopurpurin 4 B after treatment with barium mercuric iodide than before. In connection with the peculiar action of the double mercuric iodides to which we now call attention it

should be noted that Vignon (Comptes Rend., 116, 517 and 645) finds that very dilute mercuric chloride solution acts on cellulose; he considers that oxy-cellulose is produced as the result of an oxidising action represented by the equation

$$HgCl_2 + HgO = Hg_2Cl_2 + O.$$
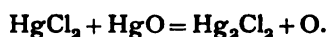
No explanation of this kind is applicable to the facts we now bring forward, because the treatment with iodides does not give rise to the formation of oxycellulose; if oxycellulose were produced the yarn would dye more strongly with basic colours than before the action of the iodide, whilst we find that the treated cotton has practically the same affinity for methylene blue as has the untreated yarn. In view of the similarity in behaviour of cotton yarn towards caustic soda and iodides, it seemed desirable to ascertain the effect upon the tensile strength of treating mercerised yarn with saturated potassium iodide solution. For this purpose a lea of the material treated with 1·342 caustic soda for 24 hours, and subsequently washed and dried, was steeped in saturated potassium iodide solution for one day, and after washing and drying was torn in the usual way. The results are summarised in Table XVI.

TABLE XVI.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
370	1	455	1	525	6
390	1	460	2	530	3
395	2	465	5	535	5
400	1	475	3	540	3
410	1	480	3	545	2
415	3	485	5	555	6
420	1	490	3	560	1
425	1	495	7	565	5
430	2	500	2	570	2
435	3	505	8	575	3
440	1	510	2	580	1
445	3	515	4	585	6
450	4	520	4	625	2

Mean tensile strength, 503·1 ± 3·3 grms. Number of observations, 118. Length broken, 5 cm. Limits of observed breaking loads, 370 and 625 grms. Ratio of same, 100 to 168·9.

The yarn, after mercerisation, had the tensile strength stated in Tables VI. and VII., viz., 524·8 ± 2·3 grms., but this, after treatment with potassium iodide, had become reduced to 503·0 ± 3·4 grms. Although potassium iodide causes a considerable increase in the tensile strength of raw cotton yarn, it effects an appreciable reduction in that of mercerised yarn. The change in the tensile strength of yarn induced by mercerisation may be, therefore, partially reversed by subsequent treatment with an iodide; and it seemed interesting to inquire whether a diminution in the tensile

strength of mercerised yarn can be also brought about by other kinds of treatment. We find that the tensile strength of mercerised yarn is considerably diminished by boiling with water. Table XVII. gives the breaking tests of a lea of material, A, which was mercerised in the same way as the hanks discussed in Tables VI. and VII., but which, after washing and drying, was boiled for six hours in a Jena glass beaker with distilled water, and dried in the air. The treatment

TABLE XVII.

Breaking Load in grms.	No.	Breaking Load in grms.	No.	Breaking Load in grms.	No.
370	2	475	5	545	4
375	1	480	7	550	3
385	2	485	1	555	1
395	1	490	2	560	1
420	2	495	5	565	4
425	1	500	9	570	6
430	1	505	3	575	4
435	6	510	3	585	1
440	2	515	2	590	2
445	1	520	9	600	1
450	3	525	2	610	2
455	1	530	2	645	1
460	3	535	5	650	1
465	4	540	3		

Mean tensile strength, $505 \cdot 0 \pm 3 \cdot 5$ grms. Number of observations, 119. Length broken, 5 cm. Limits of observed breaking loads, 370 and 650 grms. Ratio of same, 100 to 175·7.

with soda gave the yarn a tensile strength of $524 \cdot 8 \pm 2 \cdot 3$ grms., and this by the boiling with water became decreased to $505 \cdot 0 \pm 3 \cdot 5$ grms. It is interesting to note that whilst boiling with water increases the tensile strength of raw cotton yarn by about 10 per cent. (Tables II. and III.), boiling with water for six hours effects a material decrease in the tensile strength of mercerised yarn. Since the increased tensile strength resulting from mercerisation and treatment with iodides is accompanied by an increased affinity for direct colours, but with no appreciable change in the affinity for basic dyestuffs such as methylene blue, it seemed interesting to ascertain whether the tensile strength and the affinity for colouring matters changed similarly as a result of boiling the yarn with water; this is, however, not altogether the case, as is shown by the following dyeing trials made with bleached cotton yarn, which gave scarcely any oxycellulose reaction with Fehling's solution. After boiling the bleached yarn for 12 hours with distilled water in a Jena glass vessel it was found to dye much more strongly with benzopurpurin 4 B, and much less strongly with methylene blue, than before; similar, but greater, changes in affinity for the direct and the basic dyestuffs were caused by heating the bleached yarn in a sealed Jena glass tube with water at 150° for two hours. On mercerising the yarn and then

boiling it with water for 12, 24, 36, and 48 hours, the affinity for the direct colour was continuously increased, and that for the basic colour continuously decreased; the mercerised yarn was found to dye at least twice as strongly with benzopurpurin 4 B after 48 hours' boiling with water than before boiling. Although cotton yarn treated with iodide solutions in many respects resembles mercerised yarn, important differences are observed between the degree of lustre produced on immersing yarn under tension in caustic soda and iodide solutions. Yarn under tension develops a very slightly increased lustre on treatment with iodide and subsequent washing, although the same sample of yarn may become highly lustrous when mercerised under tension. The causes of this difference have been discussed in Part I. of this journal, together with the chemical behaviour of various technically important fibres towards iodides.

The quantitative results given in the previous pages may be conveniently summarised as in Table XVIII., in which the table from which the results are taken is given in the first, and the tensile strength, t, in the third column. The tensile strength, reduced to that of the material A, as a basis of 100, is stated in column 4, and the limits of measurement of t, and the ratio of those limits, are stated in columns 5 and 6. It is interesting to note that the widening of the limits of the observed tensile strengths is accompanied by a comparatively slight increase in the probable error of the mean, and that in spite of the wide limits between which the observed tensile strengths lie in many cases the probable error is never more than 0·7 per cent. It is further important to notice that when the mean tensile strength is greatly increased by the application of any chemical treatment which we have studied, considerable disturbances in the structure of the yarn took place, as is indicated by the great widening of the limits of the observed tensile strength in such cases. In the previous part of this journal we have discussed the shrinkage which results from the subjection of the standard yarn A to treatment; the lengths of the leas of yarn A before and after treatment were ascertained by hanging the lea on a hook, suspending a weight of 25 grms. from it, and measuring the length of the lea as accurately as possible with a millimetre scale. The lengths (l) in centimetres are given in column 4 of Table XIX. During the determinations of the tensile strength of the various treated yarns, observations were made of the elongation at the breaking load of each thread; these elongations vary very considerably amongst threads from the same hank, and for our present purpose it suffices to state the mean percentage elongation of the yarn at the breaking load. These numbers are stated in column 5 of Table XIX., and from the lengths of the hanks and the elongations we have calculated

Table XVIII.

	Treatment of Yarn.	Tensile strength t.	t reduced to III. as 100.	Limits of observed tensile strength.	Ratio of limits, 100 to—
II.	Raw yarn	378·0 ± 1·7	90·6 ± 0·40	330 and 440	133·3
III.	1 per cent. Na₂CO₃ solution	417·4 ± 2·1	100·0 ± 0·50	285 , 510	179·0
IV.	15 " "	419·7 ± 2·2	100·6 ± 0·53	325 , 595	155·4
V.	NaHO solution, 1 day	530·9 ± 3·8	127·2 ± 0·90	355 , 665	187·3
VI.	" " 6 days	526·3 ± 3·8	126·1 ± 0·90	400 , 675	168·7
VII.	" " "	543·9 ± 3·5	125·5 ± 0·84	355 , 700	197·2
VIII.	Raw yarn, 1 mm.	479·4 ± 3·4	114·9 ± 0·81	360 , 590	163·8
IX.	KI solution, 1 day	431·6 ± 2·3	103·4 ± 0·56	305 , 520	170·5
X.	" " 6 days	420·4 ± 2·1	100·7 ± 0·50	315 , 500	158·7
XI.	BaI₂ solution, 1 day	433·4 ± 3·0	103·8 ± 0·72	310 , 570	183·9
XII.	KI, HgI₂ solution 1 day	444·9 ± 2·9	106·6 ± 0·71	330 , 590	178·7
XIII.	" " 6 days	443·3 ± 2·7	106·2 ± 0·65	325 , 575	176·9
XIV.	BaI₂, HgI₂ solution, 1 day	534·3 ± 3·9	128·0 ± 0·92	395 , 670	169·6
XV.	" " 6 days	526·6 ± 3·3	126·1 ± 0·79	425 , 715	168·2
XVI.	VII. with KI solution	503·0 ± 3·3	120·5 ± 0·80	370 , 625	168·9
XVII.	VII. Boiled with water	505·0 ± 3·5	121·0 ± 0·84	370 , 650	175·7

Table XIX.

	Treatment of Yarn.	Mean tensile strength = t.	Length in cms. = l.	Elongation at breaking load. Per cent.	Length at breaking point = l_1.	$t \times l$.	$t \times l$ to III. as 100.	$t \times l_1$.	$t \times l_1$ to III. as 100.
III.	1 per cent. Na₂CO₃	417·4	66·0	9·29	72·1	2755	100·0	3011	100·0
IV.	15 " "	419·7	65·6	9·56	71·9	2753	99·9	3016	100·2
V.	NaHO, 1 day	530·9	45·2	28·24	58·0	2400	86·9	3077	102·2
VI.	" 6 days	526·3	44·8	27·12	57·0	2358	85·6	2997	99·6
IX.	KI, 1 day	431·6	65·0	9·83	71·4	2805	101·8	3081	102·3
X.	" 6 days	420·4	64·6	9·86	71·0	2716	98·6	2984	99·1
XII.	KI, HgI₂, 1 day	444·9	65·2	10·00	71·7	2901	105·3	3191	106·0
XIII.	" 6 days	443·3	57·3	16·35	66·7	2540	92·2	2955	98·2
XIV.	BaI₂, HgI₂, 1 day	534·3	51·3	20·52	63·0	2794	101·4	3368	111·9
XV.	" 6 days	526·6	48·9	24·62	60·9	2575	93·5	3209	106·6

the mean lengths (l_1) to which the hanks will stretch on application of the breaking load; a comparison of the values of l and l_1 shows clearly that after a yarn has been shrunk by mercerisation or other treatment and washed and dried, it cannot be stretched to its original length without breaking. Thus 66·0 cm. of raw yarn is shrunk to 45·2 cm. by mercerising without tension, washing, and drying, and on afterwards stretching the mercerised thread to the breaking point it only attains a length of 58·0 cm.; this is a result of peculiar interest in view of the fact that the 66·0 cm. thread of raw yarn could be mercerised and washed under tension, and caused to retain that length after drying as mercerised cotton. We have indicated above the great probability that the twist is the controlling factor in determining the strength of a yarn and have given evidence suggesting that for one and the same sample of yarn the tensile strength is directly proportional to the twist. The twist in the samples of yarn produced by the various kinds of treatment mentioned is naturally inversely proportional to the length l of the lea, so that if the law just suggested is also applicable to a yarn, independently of the chemical treatment which has been applied, the product of t and l should be constant throughout the series of trials now discussed, the values of $t \times l$ are given in column 7 of Table XIX. and in column 8 are stated the values of $t \times l$ reduced to the $t \times l$ value of the material A (from III.) as a basis of 100. The values in these two columns show a considerable tendency towards constancy. But it is not quite legitimate to expect constancy in the values of $t \times l$, because at the breaking point the load t is not being applied to the length l but to the length l_1; and the product $t \times l_1$ would be more likely to be the constant quantity. This value is given in column 9, and in column 10 is reduced to the $t \times l_1$ value of the standard yarn A as 100. With the exceptions of the hanks treated with potassium or barium mercuric iodides, all the $t \times l_1$ values lie between 99·1 and 102·3, that is to say they are identical within the limits of the experimental error incurred. It may thus be safely concluded that although during mercerisation a yarn shrinks by about one-third, its tensile strength remains directly proportional to the twist. It should be noted that if, on chemical treatment, the cotton fibre preserves an unaltered volume but merely changes in length, the length l is inversely proportional to the cross sectional area a of the fibre, so that $l \times a$ is equal to the constant volume. But if a given volume of material be made up into rods of different lengths and uniform thicknesses, the breaking loads of the rods will be directly proportional to the cross sectional area and inversely proportional to the length. This result is of the same form as that obtained in the present investigation. The value of a yarn for

manufacturing purposes must be to a considerable extent dependent upon the uniformity of its twist, that is to say, a yarn which will withstand the various operations of bleaching, mercerisation, dyeing, weaving, etc., without giving great trouble owing to frequent breakages must be one in which the limits of the observed tensile strengths measured on about a hundred separate threads do not lie too far apart. The limits of the observed tensile strength for the leas of differently treated yarn which we have examined are given in Table XVIII. and are conveniently discussed after reducing them to the basis of the lowest observed breaking load as 100; the quantities thus deduced, which may be termed the "ratios of the tensile strength limits," are also given in the table and will be seen to vary widely for leas which have been subjected to different treatment. Yarn No. II., in which the ratio of the limits is as 100 to 133·3, must obviously give far less trouble during weaving owing to broken threads than that numbered III., in which the ratio is as 100 to 179·0. It seems therefore that the manufacturer would derive very reliable information as to the behaviour of a yarn during the subsequent manufacturing processes from the determination of this ratio of the limits of the observed tensile strengths, or by the comparison of the mean tensile strength with the tensile strength observations lying below the mean value. The data obtained in the way which we now describe, treated by the method which we have used, affords specific information as to the strength and the variation in strength of a yarn, whilst the figures given by the lea testing machine ordinarily used are meaningless in so far as the tensile strength of the yarn is concerned.

THE JOINTING OF PIPES

for Drains and Sewers.

By Professor J. RADCLIFFE, C.E.

EARTHENWARE and stoneware pipes have long been used for the conveyance of sewage, but within the last few years considerable improvement has been made in the quality of the pipes used for that purpose. The improvement in the quality of the pipes was necessary to satisfy modern requirements, and to compete with pipes of cast-iron and other materials. Stoneware pipes have some advantages over cast-iron pipes, especially as regards the maintenance of a smooth interior surface, but frequently they lack strength, and always require a large number of joints. The supplementary strength may be obtained by using concrete, but the number of joints cannot be largely reduced, though attempts have recently been made to manufacture pipes of greater length. The result has not been altogether satisfactory. The joints of cast-iron pipes present little or no difficulty, a caulked lead and gaskin joint being quite satisfactory, except in places where great variation of temperature takes place. In such cases lead joints fail, but joints made of plain gaskin, thoroughly soaked in Portland cement and well caulked, or of rust cement with a minimum quantity of sal-ammoniac, answer the purpose quite admirably. The turned and bored joint for cast-iron pipes is not satisfactory, unless provision is made for the insertion of lead to maintain water tightness during any slight movement due to settlement, vibration, or other causes. Where rust cement is used, the protective coating must be removed from the cast-iron where the surface is to be in contact with the cement. The jointing of stoneware pipes is an important matter, and well worth the close attention of all interested in sanitation; leakage of sewage or air from the pipes may mean pollution of the soil, air, and water about human habitations. That difficulties exist in regard to this is clearly shown by the number of patent joints now on the market. Great ability and ingenuity have been exercised by the inventors, and they deserve to reap a substantial reward from their labours, but in the author's opinion the wrong trail has been followed. Instead of dealing with the form of socket on each pipe, attention should have been given to the cementing materials used in the sockets. As all are aware, clay was considered good enough for jointing earthenware pipes in bygone days. Since that time Roman cement, Medina cement and Portland cement have been largely used for the purpose. The last-mentioned is now almost universally adopted, and everyone seems satisfied that perfection has been reached, and that there is no room for improvement. My experience,

unfortunately, does not confirm this, and I ask those interested who have opportunities for observation to carefully test, by hydraulic pressure, lengths of stoneware pipe drains or sewers that have been laid over one year. I feel sure the result in many cases will disappoint the observers. One case may be mentioned. In the drainage of a very large building by stoneware pipes, the work was done by day work, the materials being of the best and supplied by well-known firms. The work was carried out in firm ground, under strict supervision and my directions. When finished the hydraulic test was applied to each length, and maintained for twenty-four hours, with satisfactory results. Two years after the work was finished the whole of the drains were re-tested under my direction, the result being a great surprise to me; only two short lengths out of about forty lengths remained watertight. The cast-iron pipes which formed one section of the scheme were found in good condition, and all the lengths were perfectly tight when severely tested. The defects in the stoneware drains were due to the expansion of the cement used for jointing purposes, long after it was supposed to be set, numerous fine cracks being clearly seen at a number of the sockets, whilst other sockets were broken. Many examples could be given, if
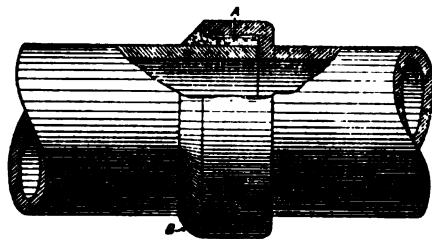
Fig. 1.

necessary, to prove the results obtained in the above case. The defects are not confined to the ordinary forms of joints, but apply equally to many patent joints for which Portland cement is used, a peculiarity being that joints made by one man with the same brand of cement, and mixed at the same time, do not all show defects. During the period of observation, which has been very extensive, a number of interesting details have been noted, some of which may be given here. In the ordinary joint, with or without gaskin, there is a tendency for the soft cement, during setting, to leave the upper part of the socket, as shown in A, and to bulge out at B, Fig. 1.

In a patent joint with a cavity, the Portland cement in the form of grout is run in and worked round with a cane or other appliance to exclude the air and entirely fill the cavity with cement. In this case

the heavy particles of the cement settled to the bottom of the joint, and left the liquid portion at the top, before setting took place. On testing this joint after 48 hours' exposure to air the upper part showed signs of leakage; on examination, the density of the cement was clearly greatest at the lower part of the joint, and may be likened to the shading of the cement in Fig. 2.
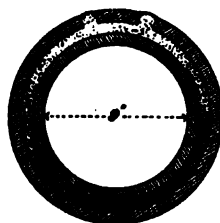
Fig. 2.

In another case, the ordinary cement joints were made with dry spigots and sockets (not dried specially); shortly after setting cracks began to develop in the cement, as was shown by the joint exhibited. The insertion of gaskin made no difference. Pipes of the same kind were soaked in water and jointed with the cement mixed for the previous example by the same workman. Though the joints have been made some time, no defects are noticeable, as was shown by examination of the joint exhibited. A remarkable feature of cement joints is the small amount of hold that the cement, when set, has upon stoneware pipes; this is clearly shown by breaking a pipe joint. In the joints without gaskin, or a substitute for it, there is great
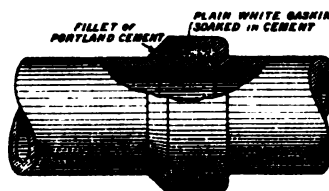
Fig. 3.

difficulty in preventing the cement, when in a soft state, passing round the end of the pipe and forming a ridge on the inside. The removal of this ridge may disturb the partly set cement in the joint, or a slight disturbance of the pipe may break the joint and cause leakage. Provision must be made to prevent this. The use of a small ring of gaskin does not reduce the strength of the joint, but a ring of fine plain gaskin, thoroughly soaked in cement, forced solid

to the end of the socket, enables a cement joint to withstand higher pressure than if cement alone were used. A joint that will withstand considerable pressure may be made by filling and caulking the socket with plain fine gaskin thoroughly soaked with liquid cement, and afterwards pointing the face of the socket, as shown in Fig. 3. A joint of this kind has been made for inspection, and will with safety withstand forty feet head of water. I cannot say what effect the gaskin has upon the life of the cement, though joints of this kind made seventeen years ago are still withstanding a constant pressure of eighteen feet head of water. With few exceptions, the joints submitted for your inspection are water-tight and gas-tight, but how long will they remain so? The answer is not easily found.

With care a cement joint may be made gas-tight and water-tight, but the action of Portland cement is so peculiar that no reliance can be placed upon it as a jointing material for stoneware pipes. As previously mentioned, the tendency to expand long after setting is the great weakness. This has done more than anything else to extend the use of cast-iron pipes for drainage purposes, as engineers (especially in America) hesitate to carry out high class work with material that may cause the work to be defective in a few years. There are no tests except those extending over a considerable period that will give reliable information on the point. All those who have experience in this class of work, know that the principal part of the cement used for this purpose is purchased by contractors in the cheapest market, and frequently in small quantities. The cement is used without the application of any test, in fact a knowledge of the specific gravity of the cement would be useless; the chemical composition of the cement would indicate nothing in the direction named, as a variation of the conditions under which two samples of the same composition are burned or calcined will cause a difference in their expansive properties; the test for tensile strength would also be useless, and the variation of temperature during setting would indicate unsoundness which aëration might remedy, but would not indicate anything as to the action of the cement some time after use. The addition of sand to the Portland cement will not remove the difficulty. The tests used to determine the amount of expansion are satisfactory, so far as they go, but they only cover the action during short periods.

Authorities almost agree that the maximum expansion after twenty-four hours' aëration should not exceed 12 millimetres; but a good sample may show an expansion of only 2 millimetres, another sample under exactly the same conditions may expand 40 millimetres. In both cases there is a total absence of proof that there will be no further expansion in the future. In several cases cement,

moulded in lengths 47·124 ins. × 3 ins. × ¼ in. (as used in the joint of a 12-in. pipe) has shown an increase in length of ¼ in. The pressure generated in a confined space by the expansion named would be difficult to ascertain accurately. In my opinion, the evidence is sufficient to justify the search for a material of less uncertain character, and I place before the meeting the result of my experience, in the hope that others will supplement it, for the benefit of those whose health depends upon the efficiency of work of the class referred to, and to prevent the expenditure of money upon work which may prove defective in a short time. In seeking to remedy defects a man naturally endeavours to obtain information regarding the experience of others, and to apply the best results to his own case. I found that coal-tar pitch had been used in several cases, and also that pitch mixed with sand and other ingredients had been employed for jointing pipes for drainage purposes, but the results had been unsatisfactory. The chief properties of material suitable for the purposes are :—

1. The cost must be reasonable.

2. Highly skilled labour must not be essential to its application.

3. The material must not fail by variation of temperature, expansion, contraction, vibration, or natural decay.

4. There must be a small amount of elasticity to prevent leakage in case of slight settlement of the ground in which the pipes are laid.

5. The material must obtain a firm hold on the surface of the pipe and socket.

6. The material must set within a reasonable time, to allow the joints to be thoroughly tested before the pipes are covered up.

During the last five years I have carried out experiments with various materials, and during that period joints made with many substances have been in use and under close observation. The best results were obtained by using sulphur and bitumen. The first-named made a sound joint when run in a molten condition into the socket or cavity, but owing to the peculiar properties of sulphur some difficulty was experienced in making the joints. The conclusion arrived at was that sulphur alone is unsatisfactory for the purpose (conditions 2, 3, 4 and 5 not being entirely satisfied). Mixtures of sulphur and bitumen have also been tried, but the tendency of the two substances to separate made it difficult to obtain a mixture of uniform consistency. The variation in the melting points of the substances added to the difficulty. It was found that at a low temperature crushed sulphur simply acted as sand in the melted bitumen;

under the best conditions obtained by mixing the two substances the result did not justify its use on a large scale, the same conditions remaining unsatisfied. Extensive experiments have been made with bitumen in various forms, including coal-tar pitch and natural rock asphalte. Materials have been supplied for the purpose by the Val de Travers Co., the Limmer Rock Asphalte Co., the Brunswick Rock Asphalte Co., and others. The results were such as to justify further and extensive trials; two important points were clearly shown, namely, that coal-tar pitch alone is unsuitable for the purpose, and that other forms of bitumen mixed with an excessive quantity of oil should not be used. In both cases a creeping action is set up at ordinary temperature, so that in soft ground the ordinary socket of a pipe may be practically emptied by this action. Fig. 4 shows the
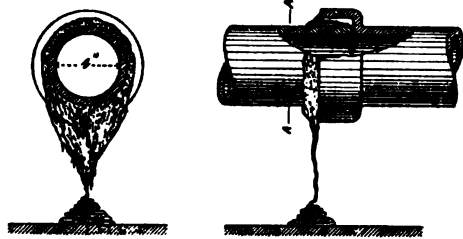
Section through A A.   Fig. 4.

action referred to, and a joint of this material was available for inspection. A mass of the same material creeping over a glass plate was also shown. This action is the principal one to be observed and prevented. No difficulty need be experienced in detecting faulty material of this kind. The low melting-point would indicate an excess of oil, or the slow setting and lack of hardness of a small quantity of the heated substance when allowed to cool in air or when placed in cold water would give the same information. The simple tests referred to may be easily applied by a drainage inspector in a very short time, without special appliances. The best results were obtained by carefully heating three parts of natural rock asphalte (hard mastic) with the addition of one part of coal-tar pitch and one part of fine clean sand (the pitch and sand were heated and mixed before being placed in the asphalte); the pitch caused the heated mass to liquefy sufficiently to run into the joints of the pipes (ordinary and patent). A simple arrangement for comparing samples of the material as regards their power to resist softening influences was shown. Pieces of material of equal weight are suspended in

glass beakers containing cold water, the temperature is slowly raised to boiling point, and the result carefully noted as follows:—

No. 1 sample.   Time.
    Temperature of water and material.... 12° C. ...   —
    Material becomes plastic .... 30° C. ...   40min.
        „   commences to creep .... 41° C. ... 1hr. 0min.
        „   melts .... 80° C. ... 1hr. 30min.

No. 2 sample.
    Temperature of water and material.... 12° C. ...   —
    Material becomes plastic................. 35° C. ...   38min.
        „   commences to creep............ 65° C. ... 1hr. 8min.
        „   melts .... 95° C. ... 1hr. 23min.

No. 3 sample.
    Temperature of water and material.... 12·5° C. ...   —
    Material becomes plastic .... 25° C. ...   35min.
        „   commences to creep............ 35° C. ...   50min.
        „   melts .... 65° C. ... 1hr. 5min.

No. 4 sample.
    Temperature of water and material.... 14° C. ...   —
    Material becomes plastic (slight) ...... 75° C. ...   35min.
    No creeping action .... 100° C.⎫
    No melting action .... 100° C ⎬... 1hr. 0min.

No. 5 sample.
    Temperature of water and material .... 13° C. ...   —
    Material becomes plastic (slight) ...... 85° C. ...   33min.
    No creeping action .... 100° C.⎫
    No melting action .... 100° C.⎬... 1hr. 0min.

The principal point requiring attention is the temperature at which the material creeps. This should be as high as possible; material that only creeps at high temperature shows a clean fracture in section when broken, as shown by the broken samples prepared for inspection. The material referred to satisfied the conditions previously mentioned in the paper, so far as the author has been able to ascertain. The cost is reasonable, and in many cases much less than Portland cement, when all matters are taken into consideration, as there need be no waste; the trench need not remain open, as with cement when waiting for the cement to set sufficiently hard to enable tests to be applied. A defect in a joint may be quickly made good by using a plumber's lamp or hot iron. In work recently carried out there was a considerable saving of time, and few joints leaked when

under a very sensitive hydraulic test. Highly skilled labour is not required in its application, the ordinary drain layer is fully qualified to make the joints. The practical application of the material on a large scale for jointing purposes has shown to the author's satisfaction that, with proper care in the preparation of the material, there will be no failure due to variation of temperature, expansion, contraction, vibration, or natural decay. The lengths of pipe placed before the meeting for inspection were jointed over three years ago, and now contain compressed air at a pressure of 4 pounds per square inch without leakage. The pipes were not made specially for this test, but were supplied as material for a large drainage scheme. The pipes are fitted with Button's patent joint. A peculiar and unusual circumstance occurred during the laying of a line of 12″ pipes, jointed by bitumen in this form, and which served to illustrate the existence of elasticity in the cementing material. The pipes were laid and jointed ready for testing on Saturday noon. They were secured at the lowest end by the joints to a large fireclay chamber bottom, the chamber being built of the best blue brick in cement mortar. The testing plugs were inserted in the pipes and left until Monday morning. The workmen then found the trench containing the pipe filled with rainwater, and the loose end of the pipe floating near the surface of the water. The clerk of works expected that the joints would require to be remade, but, to his surprise, when the water was
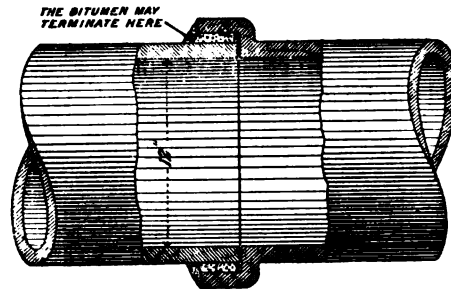
Fig. 5.

pumped out of the trench, and the pipe settled down, on the application of the hydraulic test the joints were found uninjured, and passed as satisfactory by the clerk of works. A very great weakness of ordinary cementing material is the insecure hold which it obtains on the surface of the pipe or socket, especially if the surface is slightly glazed. Bitumen, if properly applied, overcomes this difficulty to a considerable extent; but if the cavity or spigot and socket is coated with a film of the heated material, the hold secured by the material

on the pipe is in some cases much greater, and the efficiency of the joint is increased. It is important in almost all cases that the pipes should be tested before they are covered with earth. Frequently great inconvenience is experienced by having to leave trenches open for a sufficient time to allow the jointing material to set, and to repair defective joints. Bitumen removes this difficulty, as joints made of this substance may be tested under a considerable head of water in less than one hour after the joints are made. The material under consideration is not only suitable for the joints of small pipes, but pipes of large diameter may be jointed by it. A 12-in. pipe joint was prepared (in the manner previously described) for inspection (Fig. 5). In the case of large joints it is advisable to use a pan with a valve in the bottom, so that the joints may be run without break, as the material is very like lead when brought into contact with cold surfaces, and sets quickly. For ordinary joints on pipes up to nine inches diameter a clay fillet is satisfactory for running the joints, but above that size clips (as used for cast-iron water-pipe joints) are best. The heavier parts of the bitumen should not be allowed to settle to the bottom of the pan in which the material is heated. I would like it to be clearly understood that the best results of experiments carried out in the laboratory, and previously referred to, have been applied and thoroughly tested in actual work. In a scheme completed two years ago at a cost of over £8,000, pipes varying in diameter from four inches to twelve inches were all jointed by bitumen of the kind mentioned with very great success. I have endeavoured to obtain a material that may be used (without extra cost) for ordinary or patent joints, that will not possess the uncertain properties of Portland cement when used for jointing pipes for drains and sewers.

Asymmetric Optically Active Selenium

compounds and the sexavalency of selenium and sulphur. d- and l-phenylmethylselenetine salts.

By Prof. W. J. POPE, F.R.S., and ALLEN NEVILLE, B.Sc.

THE fact that amorphous substances can exhibit optical activity as a result of the presence in the molecule of asymmetric atoms other than those of carbon having been placed beyond question by the work of Pope, Peachey, and Harvey (Trans. Chem. Soc., 1899, 75, 1127; 1900, 77, 1072; 1901, 79, 828), it is important that the results obtained by these authors should be extended to compounds of as large a number of elements as possible, as the foundation would thus be laid for a general stereochemical scheme which would embrace all the elements. For this reason we have investigated substances containing an asymmetric quadrivalent selenium atom and, in the present paper, contribute results proving that such an atom has a tetrahedral environment and gives rise to optical activity. For the purposes of this investigation a mixed alkyl selenide was naturally required, and methods for the preparation of such substances not having been previously devised, it was proposed to prepare methyl ethyl selenide by a series of steps sufficiently indicated by the following scheme :

$(C_2H_5)_2Se \rightarrow C_2H_5 \cdot Se \cdot Se \cdot C_2H_5 \rightarrow C_2H_5 \cdot Se \cdot Na \rightarrow C_2H_5 \cdot Se \cdot CH_3$.
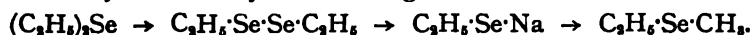
Although we procceded far enough with this course to ascertain definitely that it would lead to success, it was found that the manipulation of large quantities of the volatile diethyl diselenide, unless performed with irksome precautions, gave rise to unpleasant physiological symptoms in the operator; this plan of attack was therefore abandoned in favour of one based on the following considerations. The difficulties encountered in dealing with the dialkyl selenides are due to their volatility and might be avoided by the use of a selenide of high molecular weight, provided that such a substance had, in other respects, the necessary properties; that is to say, if phenyl methyl selenide, prepared by the following series of steps :

$(C_6H_5)_2Se \rightarrow C_6H_5 \cdot Se \cdot Se \cdot C_6H_5 \rightarrow C_6H_5 \cdot Se \cdot Na \rightarrow C_6H_5 \cdot Se \cdot CH_3$,
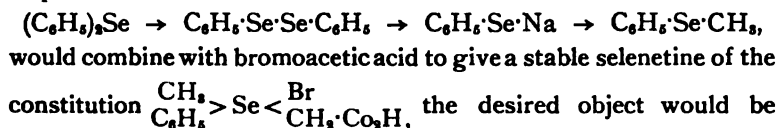
would combine with bromoacetic acid to give a stable selenetine of the constitution $\frac{CH_3}{C_6H_5} > Se < \frac{Br}{CH_2 \cdot Co_2H}$, the desired object would be attained. Although phenyl methyl sulphide is quite inert towards bromoacetic acid, it was thought probable that, since the oxygen in alkyl oxides exhibits more reluctance than the sulphur in alkyl sulphides to become quadrivalent, the selenium in alkyl selenides might have so great a tendency to become quadrivalent as to

counteract the inhibiting influence of a phenyl group and so cause phenyl methyl selenide to combine readily with bromoacetic acid. This surmise proved correct, and a striking illustration is thus furnished of the periodic gradation in the ease with which bivalent oxygen, sulphur, and selenium become quadrivalent. The only selenetine previously described is that prepared from diethyl selenide and bromoacetic acid by Carrara (*Gazzetta*, 1894, 24, ii, 173); this author, however, gives no data from which an opinion can be formed as to the relative stability of the thetines and selenetines. It is important to note in this connection that whilst an aqueous solution of diethylthetine bromide evolves a strong odour of ethyl sulphide during evaporation on the water-bath, phenylmethyl-selenetine bromide remains practically odourless under similar conditions; although the latter substance contains the highly acidic phenyl group, the basic character of the quadrivalent selenium atom imparts great stability to the selenetine.

Phenyl Methyl Selenide, $C_6H_5 \cdot Se \cdot CH_3$.

Diphenylsulphone is converted into diphenyl selenide and the latter into diphenyl diselenide by the convenient method given by Krafft and Lyons (*Ber.*, 1894, 27, 1761); the diselenide (1 mol.) is converted into sodiophenyl selenide by adding sodium wire to its absolute alcoholic solution and, on running in methyl iodide (2 mols.), vigorous action ensues with formation of phenyl methyl selenide and separation of sodium iodide. After distilling off most of the alcohol, treating with water, and extracting with ether, the ethereal solution is dried over potash and distilled; a good yield of phenyl methyl selenide is obtained as a pale yellow oil which boils at 200-201° without decomposition, and has a not unpleasant aromatic, garlic-like odour :

$0 \cdot 1623$ gave $0 \cdot 2922$ CO_2 and $0 \cdot 0684$ H_2O. $C = 49 \cdot 04$; $H = 4 \cdot 68$.

C_7H_8Se requires $C = 49 \cdot 12$; $H = 4 \cdot 67$ per cent.

Phenyl methyl selenide is the first mixed alkyl selenide which has been described, and seems to be much more stable in the air than the phenyl hydrogen selenide prepared by Krafft and Lyons (*loc. cit.*).

Phenylmethylselenetine Bromide, $\dfrac{CH_3}{C_6H_5} > Se < \dfrac{Br}{CH_2 \cdot CO_2H}$

On warming a mixture of phenyl methyl selenide and bromoacetic acid in molecular proportion on the water-bath, combination takes place rapidly with development of heat and formation of a white, crystalline mass; after crystallisation from a mixture of ether and alcohol, the selenetine bromide is obtained in white crystalline

scales melting at $111°$. It is very soluble in water or alcohol, but practically insoluble in ether :

o·1554 gave o·1985 CO_2 and o·0504 H_2O. C = 34·81; H = 3·60.

o·3400 „ o·08772 Br with standard $AgNO_3$. Br = 25·80.

$C_9H_{11}O_2BrSe$ requires C = 34·83; H = 3·54; Br = 25·81 per cent.

Resolution of Externally Compensated Phenylmethylselenetine Bromide.

On exactly precipitating externally compensated phenylmethyl-selenetine bromide with silver d-bromocamphorsulphonate in hot aqueous solution, filtering off the silver bromide and evaporating the filtrate to dryness, a white crystalline residue is obtained; this is systematically fractionally crystallised from absolute alcohol, the less soluble fractions being passed in one direction through a series of beakers, whilst the more soluble portions proceed in the opposite direction. The least soluble constituent is d-phenylmethylselenetine d-bromocamphorsulphonate (d-B, d-A), and separates from alcohol in small, colourless, rectangular tablets melting at $168°$. The crystals apparently belong to the orthorhombic system and exhibit the forms (001), (101), and (011); the form (001) is predominant, the c-axis is the acute bisectrix, and the optic axial plane is a(100). The optic axial angle is large, and the double refraction is positive in sign :

o·1511 gave o·2336 CO_2 and o·0630 H_2O. C = 42·15; H = 4·63.

$C_{19}H_{26}O_6BrSSe$ requires C = 42·22; H = 4·62 per cent.

The proof of the purity of the salt and the final determination of its optical constants are given by the following measurements of the rotatory powers of three consecutive fractions obtained on crystallising it from alcohol :

(1) o·2216 gram, made up to 25 c.c. with water, gave a_R + 1·09° in a 2 dcm. tube; whence $[a]_D$ + 61·5° and $[M]_D$ + 332·0°.

(2) o·2528 gram, made up to 25 c.c. with water, gave a_D + 1·24° in a 2 dcm. tube; whence $[a]_D$ + 61·3° and $[M]_D$ + 331·1°.

(3) o·2356 gram, made up to 25 c.c. with water, gave a_D + 1·15° in a 2 dcm. tube; whence $[a]_D$ + 61·0° and $[M]_D$ + 329·5°.

The mean values $[a]_D$ + 61·26° and $[M]_D$ + 330·8° are thus obtained, and since the molecular rotatory power of the d-bromocamphorsul-phonic ion in aqueous solution is $[M]_D$ + 270·0°, it follows that the corresponding value for the d-phenylmethylselenetine ion is $[M]_D$ + 60·8°.

After separating the d-phenylmethylselenetine d-bromocamphor-sulphonate as far as possible, there remains a very soluble residue

which has a tendency to become gummy, but by repeated crystallisation from water l-phenylmethylselenetine d-bromocamphorsulphonate is obtained in minute white scales. It is finally purified by crystallisation from alcohol, and forms aggregates of colourless needles melting at $151°$:

0·1613 gave 0·2493 CO_2 and 0·0671 H_2O.   C = 42·09; H = 4·58.

$C_{19}H_{25}O_6BrSSe$ requires C = 42·22; H = 4·62 per cent.

The purity of this material was proved and its rotatory constants were ascertained, by the following determinations of the rotatory power of three consecutive fractions :

(1) 0·2461 gram, made up to 25 c.c. with water, gave a_D + 0·76° in a 2 dcm. tube; whence $[a]_D$ + 38·6° and $[M]_D$ + 208·4°.

(2) 0·2371 gram, made up to 25 c.c. with water, gave a_D + 0·74° in a 2 dcm. tube; whence $[a]_D$ + 39·0° and $[M]_D$ + 210·7°.

(3) 0·2511 gram, made up to 25 c.c. with water, gave a_D + 0·78° in a 2 dcm. tube; whence $[a]_D$ + 38·8° and $[M]_D$ + 209·7°.

The mean values $[a]_D$ + 38·81° and $[M]_D$ + 209·6° are thus obtained, and, taking $[M]_D$ + 270·0° for the d-bromocamphorsulphonic ion, the molecular rotatory power of the l-phenylmethylselenetine ion is calculated as $[M]_D$ − 60·4°, a number which agrees very closely with the value $[M]_D$ + 60·8° obtained above for the enantiomorphously related ion.

d- and l-*Phenylmethylselenetine Platinichlorides,*

$$\left({CH_3 \atop C_6H_5} > Se < {Cl \atop CH_2 \cdot CO_2H} \right)_2, PtCl_4.$$

On adding a cold alcoholic solution of platinic chloride to an alcoholic solution of either of the above d-bromocamphorsulphonates containing a little hydrochloric acid, the corresponding platinichloride slowly separates as a microcrystalline yellow powder; the platinichlorides are insoluble in water or alcohol, but very soluble in acetone, and crystallise from a hot mixture of acetone and water in minute yellow prisms melting at $171°$. The first of the appended analyses was made on d-phenylmethylselenetine platinichloride, and the second on its enantiomorphously related isomeride :

(1) 0·1835 gave 0·1672 CO_2 and 0·0414 H_2O.   C = 24·85; H = 2·50.

(2) 0·1923 „ 0·1752 CO_2 „ 0·0432 H_2O.   C = 24·80; H = 2·49.

$C_{18}H_{22}O_4Cl_6PtSe_2$ requires C = 24·88; H = 2·53 per cent.

Three successive fractions from the crystallisation of the d-platinichloride gave the following determinations of rotatory power :

(1) 0·5124 gram, made up to 25 c.c. with acetone, gave a_D + 0·26° in a 2 dcm. tube; whence $[a]_D$ + 6·3° and $[M]_D$ + 55·0°.

(2) 0·5561 gram, made up to 25 c.c. with acetone, gave a_D + 0.28° in a 2 dcm. tube; whence $[a]_D$ + 6·3° and $[M]_D$ + 54·6.

(3) 0·5474 gram, made up to 25 c.c. with acetone, gave a_D + 0·28° in a 2 dcm. tube; whence $[a]_D$ + 6·4° and $[M]_D$ + 55·5°.

The mean values are thus $[a]_D$ + 6·34° and $[M]_D$ + 55·0°. A similar set of three values was also obtained from consecutive fractions of the enantiomorphously related isomeride.

(1) 0·6124 gram, made up to 25 c.c. with acetone, gave a_D − 0·31° in a 2 dcm. tube; whence $[a]_D$ − 6·3° and $[M]_D$ − 54·8°.

(2) 0·5225 gram, made up to 25 c.c. with acetone, gave a_D − 0·26° in a 2 dcm. tube; whence $[a]_D$ − 6·2° and $[M]_D$ − 54·0°.

(3) 0·4812 gram, made up to 25 c.c. with acetone, gave a_D − 0·24° in a 2 dcm. tube; whence $[a]_D$ − 6·2 and $[M]_D$ − 54·1°.

The mean values, namely, $[a]_D$ − 6·25° and $[M]_D$ − 54·3°, are in close numerical agreement with those obtained for the enantiomorphously related isomeride. The preparation in a pure state of these optically active platinichlorides containing no asymmetric carbon atoms completes the proof that the presence of an asymmetric quadrivalent selenium atom causes optical activity.

Phenylmethylselenetine Mercuriodide $\dfrac{CH_s}{C_6H_6} > Se < \dfrac{I}{CH_3 \cdot CO_2H, HgI_2}$

On adding a concentrated aqueous potassium iodide solution of mercuric iodide (1 mol.), to one of either d- or l-phenylmethylselenetine d-bromocamphorsulphonate or of externally compensated phenylmethylselenetine bromide (1 mol.), the optically inactive mercuriodide separates quantitatively as a flocculent white powder; after crystallisation from dilute alcohol, it is obtained in colourless crystalline scales melting at 141-142°. The substance is freely soluble in acetone, less so in alcohol and practically insoluble in water or ether. The polarimetric examination of this salt in acetone solution showed it to be optically inactive although prepared from a salt of the pure optically active selenetine, and on making a number of preparations of the mercuriodide from d- and l-phenyl-methylselenetine d-bromocamphorsulphonate and from the externally compensated bromide, it was found that the same substance is produced from each of these three materials; the salts from the three sources are optically inactive, have the same microcrystalline properties, and no change of melting point results on mixing any two of them. This result is a very remarkable one, because Pope and Harvey showed (*loc. cit.*) that no optical inversion attends the formation of d- or l-benzylphenylallylmethylammonium mercuriodide from its constituent salts, and Pope and Peachey (Trans. Chem. Soc., 1900, 77,

1072) showed that no racemisation takes place during the formation of *d*-methylethylthetine platinichloride, whilst in the present paper it is shown that the *d*- and *l*-phenylmethylselentine platinichlorides are still optically active; optical inversion therefore is not an invariable accompaniment to the formation of a double salt or salt of a complex acid. In order to preclude the possibility that the selenetine mercuriodides described above are really optically active, but have very small specific rotatory powers and as the observation of the racemisation of the mercuriodides should have important bearings on the constitution of such substances and on the valency of sulphur and selenium, it seemed desirable to prepare and examine the mercuriodides of an optically active sulphonium base. For this purpose we selected the *d*- and *l*-methylethylphenacylthetine *d*-bromocamphorsulphonates prepared by Smiles (Trans., 1900, 77, 1174) rather than the *d*-methylethylthetine *d*-bromocamphorsulphonate previously described by Pope and Peachey (*loc. cit.*), considering the higher rotatory powers exhibited by the former substances as likely to facilitate the investigation. On repeating Smiles's work, much higher values were obtained for the rotation constants than were given by him, and it is hence to be concluded that he did not succeed in obtaining the active thetine salts in a state of purity. We find that *l*-methylethylphenacylthetine *d*-bromocamphorsulphonate melts at 196°, and four consecutive fractions of the carefully purified salt gave the following determinations of rotatory power :

(1) 0·3545 gram, made up to 25 c.c. with water, gave a_D + 1°10' in a 2 dcm. tube; whence $[a]_D$ + 41·1° and $[M]_D$ + 207·6°.

(2) 0·4288 gram, made up to 25 c.c. with water, gave a_D + 1°26' in a 2 dcm. tube; whence $[a]_D$ + 41·8° and $[M]_D$ + 210·9°.

(3) 0·3836 gram, made up to 25 c.c. with water, gave a_D + 1°18' in a 2 dcm. tube; whence $[a]_D$ + 42·4° and $[M]_D$ + 213·9°.

(4) 0.4109 gram, made up to 25 c.c. with water, gave a_D + 1°22' in a 2 dcm. tube; whence $[a]_D$ + 41·5° and $[M]_D$ + 209·8°.

The mean values for the salt are $[a]_D$ + 41·7° and $[M]_D$ + 210·6°.

d-Methylethylphenacylthetine *d*-bromocamphorsulphonate melts at 180-181°, and two consecutive fractions of the salt gave the following results :

(1) 0·4714 gram, made up to 25 c.c. with water, gave a_D + 2°29' in a 2 dcm. tube; whence $[a]_D$ + 65·8° and $[M]_D$ + 332·5°.

(2) 0·3525 gram, made up to 25 c.c. with water, gave a_D + 1°52' in a 2 dcm. tube; whence $[a]_D$ + 66·0° and $[M]_D$ + 333·2°.

The mean values are thus $[a]_D$ + 65·9° and $[M]_D$ + 332·8°.

The molecular rotatory power of the optically active methylethyl-phenacylthetine ion in aqueous solution, calculated as one-half the difference of the values for the d-bromocamphorsulphonate of the d- and l-bases, is thus: $[M]_D = \pm (332\cdot8/2 - 210\cdot6/2) = \pm 61\cdot1°$; the value calculated from Smiles's results, namely, $[M]_D \pm 19\cdot4°$, is less than one-third of this. The d- and l-methylethylphenacylthetine picrates, prepared from the corresponding d-bromocamphorsul-phonates, were fractionally crystallised from acetone and the rotatory powers of two successive fractions of each determined with the following results :

d-*Methylethylphenacylthetine Picrate.*

(1) 0·4512 gram, made up to 25 c.c. with acetone, gave $a_D + 0°21'$ in a 2 dcm. tube; whence $[a]_D + 9\cdot7°$ and $[M]_D + 41\cdot3°$.

0·5121 gram, made up to 25 c.c. with alcohol, gave $a_D + 0°20'$ in a 2 dcm. tube; whence $[a]_D + 8\cdot1°$ and $[M]_D + 34\cdot6$.

(2) 0·3912 gram, made up to 25 c.c. with acetone, gave $a_D + 0°18'$ in a 2 dcm. tube; whence $[a]_D + 9\cdot6°$ and $[M]_D + 40\cdot8°$.

0·4411 gram, made up to 25 c.c. with alcohol, gave $a_D + 0°17'$ in a 2 dcm. tube; whence $[a]_D + 8\cdot0°$ and $[M]_D + 34\cdot2°$.

l-*Methylethylphenacylthetine Picrate.*

(1) 0·4912 gram, made up to 25 c.c. with acetone, gave $a_D - 0°23'$ in a 2 dcm. tube; whence $[a]_D - 9\cdot7°$ and $[M]_D - 41\cdot5°$.

0·4512 gram made up to 25 c.c. with alcohol, gave $a_D - 0°18'$ in a 2 dcm. tube; whence $[a]_D - 8\cdot3°$ and $[M]_D - 35\cdot4°$.

(2) 0·4775 gram, made up to 25 c.c. with acetone, gave $a_D - 0°23'$ in a 2 dcm. tube; whence $[a]_D - 10.0°$ and $[M]_D - 42\cdot7°$.

0·4621 gram, made up to 25 c.c. with alcohol, gave $a_D - 0°19'$ in a 2 dcm. tube; whence $[a]_D - 8\cdot5°$ and $[M]_D - 36\cdot4°$.

d-Methylethylphenacylthetine picrate thus gave the mean values $[a]_D + 9\cdot63°$ and $[M]_D + 41\cdot1°$ in acetone solution, and $[a]_D + 8\cdot06°$ and $[M]_D + 34\cdot4°$ in absolute alcoholic solution. The enantiomor-phously related salt gives $[a]_D - 9\cdot88°$ and $[M]_D - 42\cdot1°$ in acetone, and $[a]_D - 8\cdot42°$ and $[M]_D - 35\cdot9°$ in alcohol.

l-*Methylethylphenacylthetine Platinichloride,*

$$\left(\begin{array}{c} CH_3 \\ C_2H_5 \end{array} > S < \begin{array}{c} Cl \\ CH_2 \cdot CO \cdot C_6H_5 \end{array}\right)_2 PtCl_4.$$

This salt is obtained in golden-yellow scales melting at 184°, on crystallising from dilute acetone the precipitate formed on adding acidified platinic chloride solution to the corresponding d-bromo-

camphorsulphonate; it is very sparingly soluble in the ordinary solvents :

0·2412 gave 0·0584 Pt. Pt = 24·62.

$C_{22}H_{30}O_2Cl_6S_2Pt$ requires Pt = 24·43 per cent.

0·2112 gram, made up to 50 c.c. with concentrated hydrochloric acid, gave a_D — 0·13° in a 4 dcm. tube; whence $[a]_D$ — 7·7° and $[M]_D$ — 61·4°. It is thus evident that the formation of the platinichloride is not accompanied by optical inversion.

Methylethylphenacylthetine Mercuriodide,

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > S < \begin{matrix} I \\ CH_2 \cdot CO \cdot C_6H_5, HgI_2. \end{matrix}$$

On adding a concentrated solution of mercuric iodide (1 mol.) in aqueous potassium iodide to one of d- or l-methylethylphenacylthetine d-bromocamphorsulphonate or of externally compensated methylethylphenacylthetine bromide (1 mol.), the optically inactive mercuriodide is precipitated. It is insoluble in benzene, ethyl acetate, or water, but crystallises from acetone or dilute alcohol in small, colourless scales melting at 128°. A number of preparations were polarimetrically examined in acetone solution, but all were optically inactive :

0·3256 gave 0·1922 HgI_2. HgI_2 = 59·02.

0·1615 „ 0·0920 HgI_2. HgI_2 = 57·94.

$C_{11}H_{15}OI_2SHg$ requires HgI_2 = 58·50 per cent.

Methylethylphenacylthetine Mercurichloride,

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > S < \begin{matrix} Cl \\ CH_2 \cdot CO \cdot C_6H_5, HgCl_2. \end{matrix}$$

The optically inactive mercurichloride is prepared by adding an aqueous solution of potassium chloride and mercuric chloride to one of a salt of the d-, l-, or externally compensated thetine, and crystallising the precipitate from dilute alcohol; it forms glistening white scales melting at 119°, and is insoluble in water or ether but dissolves in alcohol or acetone. The preparations obtained from the three sources were identical and were optically inactive in acetone solution :

0.2162 gave 0·0464 Cl on titration. Cl = 21·46.

0·3114 „ 0·0669 Cl „   Cl = 21·48.

$C_{11}H_{15}OCl_2SHg$ requires Cl = 21·23 per cent.

The fact that methylethylphenylselenetine mercuriodide and methylethylphenacylthetine mercuriodide and mercurichloride are all three obtained as optically inactive substances from salts of the optically active selenetine or thetine must be regarded as proof that optical

inversion actually does take place during their formation, for it can hardly be supposed that the three different substances are really optically active but happen to possess specific rotatory powers so small as to have evaded detection. The non-occurrence of optical inversion when d- and l-benzylphenylallylmethylammonium salts are converted into their mercuriodides led Pope and Harvey (Trans., 1901, 79, 840) to regard as improbable the suggestion that nitrogen is septavalent in such compounds and also, by analogy, that the sulphur in sulphonium mercuriodides is sexavalent; the facts now brought forward, however, necessitate a revision of this view. If, as was suggested by Smiles for the sulphonium mercuriodides (Trans., 1900, 77, 160), the quadrivalent sulphur or selenium atom in sulphonium or selenonium salts become sexavalent during the formation of the mercuriodides, the latter have the following constitutions :

$$
\begin{array}{ccc}
\mathrm{I}\diagdown \quad \diagup\mathrm{CH_3} & & \mathrm{I}\diagdown \quad \diagup\mathrm{CH_3} \\
\mathrm{I}{-}\mathrm{S}{<}\mathrm{C_2H_5} & \text{and} & \mathrm{I}{-}\mathrm{Se}{<}\mathrm{C_6H_5} \\
\mathrm{IHg}\diagup \quad \diagdown\mathrm{CH_2\cdot CO\cdot C_6H_5} & & \mathrm{IHg}\diagup \quad \diagdown\mathrm{CH_2\cdot CO_2H}
\end{array}
$$
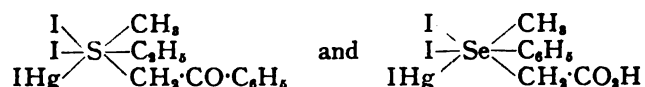
The simplest environment of the sexavalent atom would be one in which the six atomic groups are situated on three lines drawn at right angles to each other through the sexavalent atom, the six groups being thus situated at the apices of an octahedron of which the sexavalent atom occupies the centre. The most symmetrical manner in which the two new atomic groups can enter the original tetrahedral configuration during its conversion into the octahedral one results in their occupying diametrically opposite vertices of the octahedron, and if this occurs, the four groups a, b, c, and i, which are originally tetrahedrally distributed (Fig. 1) necessarily fall into the same plane as the central sulphur or selenium atom at the moment when the two new groups, i and h, become joined on (Fig. 2). But as the groups a, b, c, and i fall into a plane with the sulphur or selenium atom, the enantiomorphism due to their distribution simultaneously disappears and an optically inactive product would therefore probably result. A less symmetrical method of inserting the two groups, i and h, in the original compound, which leads, however, to an octahedral configuration of higher symmetry than Fig. 2, is illustrated by Fig. 3; this is a non-enantiomorphous configuration, and if it represents the mercuriodides, the latter would necessarily be optically inactive. The other possible configurations of the sexavalent sulphur or selenium compounds need not be now discussed; in their formation the groups h and i require to be inserted in a very unsymmetrical manner and the product would have a highly unsymmetrical configuration. That they should be produced seems improbable in view of the tendency towards the formation of

symmetrical products in chemical reactions. During the conversion of a quinquevalent into a septavalent nitrogen atom, unless in the resulting substance the original five groups lie in the same plane as the nitrogen atom, there is no reason to expect the five groups to lose their enantiomorphous arrangement or for the two new atomic groups to assume such positions in the molecule as to give rise to a non-enantiomorphous product; these are the two cases analogous to those illustrated in Figs. 2 and 3. Although the intramolecular disturbance attending a change of valency might be expected to cause optical inversion, there is no reason to anticipate the existence of a non-enantiomorphous configuration at any moment during the formation of a septavalent nitrogen compound from an optically active substituted ammonium salt, if the transition from quinque- to septa-valency occurs by some orderly series of mechanical steps. We know, in fact, that the asymmetric ammonium iodides preserve their optical activity during formation of the mercuriodides. The explanation thus offered seems rational and involves the principle enunciated by Pope and Harvey (loc. cit.), that during a change of valency the valency directions may change. Since the evidence now brought forward inclines us not to regard the above mercuriodides as salts of the complex acid $HHgI_3$ whilst we still consider the platinichlorides as salts of the acid H_2PtCl_6, it seemed desirable to attempt some experimental discrimination between the configurations represented in Figs. 2 and 3. If the acid $HHgI_3$ is not a factor in determining the formation of the mercuriodides, the production of these salts would seem due to the use of a *mercuric* compound and the particular acidic groups associated with the metal would not be so likely to influence the formation of a sexavalent sulphur compound; it should therefore be possible to prepare salts corresponding to the mercuriodides and mercurichlorides in which the three halogen groups are replaced by three optically active acidic groups. Then, if the new salt have the configuration given in Fig. 2, or if it be merely a salt of the acid $HHgX_3$ (X being the optically active group), fractional crystallisation should show it to be a mixture of the two substances (d-B, d-A, Hg2d-A) and (l-B, d-A, Hg2d-A), whilst if Fig. 3 represent the constitution and configuration of the new salt, the latter must be a single substance, potentially irresolvable, and its molecular rotatory power in aqueous solution should be of the order of thrice that of the optically active acid ion. The view taken above of the constitution of the mercuriodides is supported by the fact that we were able to prepare the following salt.

Methylethylphenacylthetine Mercuri-d-bromocamphorsulphonate,

$$S(CH_3)(C_2H_5)(CH_2 \cdot CO \cdot C_6H_5)(C_{10}H_{14}OBr \cdot SO_3H)_2Hg \cdot C_{10}H_{14}$$
$$OBr \cdot SO_4H.$$

On adding a concentrated solution of mercuric oxide in d-bromo-camphorsulphonic acid to an aqueous solution of l-methylethylphen-acylthetine d-bromocamphorsulphonate, a white precipitate is produced which, after crystallisation from dilute alcohol, is obtained in minute, white scales decomposing at about 180°; it is insoluble in ether or chloroform, but sparingly soluble in water, acetone, or alcohol :

0.4512 gave 0.07855 HgS.   Hg $= 14.98$.

$C_{41}H_{67}O_{13}Br_3S_4Hg$ requires Hg $= 15.23$ per cent.
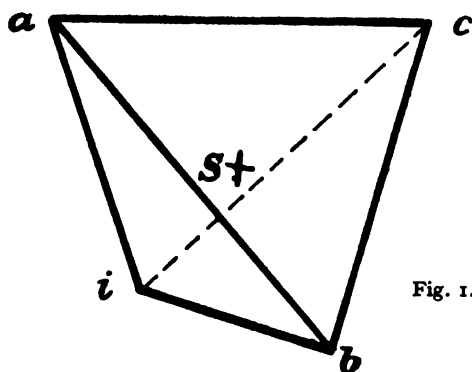
Fig. 1.
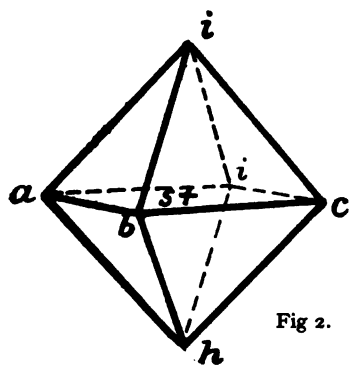
Fig 2.
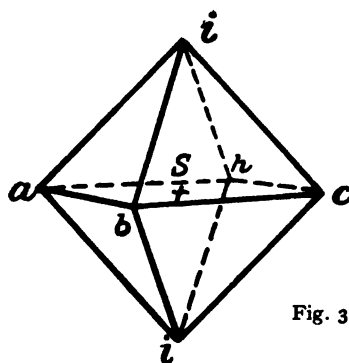
Fig. 3.

After several recrystallisations, 0.3300 gram, made up to 25 c.c. with water, gave $a_D + 1°37'$ in a 2 dcm. tube; whence $[a]_D + 60.9°$ and $[M]_D + 800°$. Within the limits of experimental error, this value is equal to $+ 810°$, three times the molecular rotatory power

of the d-bromocamphorsulphonic ion. A preparation made from d-methylethylphenacylthetine d-bromocamphorsulphonate after careful purification proved to be identical with the foregoing. 0·3512 gram, made up to 25 c.c. with water, gave a_D + 1°43′ in a 2 dcm. tube, whence $[a]_D$ + 60·8° and $[M]_D$ + 798°.

Although further investigation of this salt is needed and is now in progress, the facts that the preparations from the d- and l-thetine salts yield fractions having practically the same rotatory power, and that that rotatory power is very nearly thrice the molecular rotatory power of the optically active acid ion, indicate that the two sources yield the same and a single irresolvable product, and that the sexavalent sulphur atom is not a centre of optical activity because it contributes no appreciable amount to the molecular rotatory power of the mercuri-d-bromocamphorsulphonate. The configuration of the thetine and selenetine mercuriodides and mercurichlorides would therefore seem to be that illustrated in Fig. 3.

Volumetric Process for the Estimation of Azo Dyes, Nitro Compounds, &c.

By Professor EDMUND KNECHT, Ph.D., F.I.C.

THE valuation of the individual members of so important a class of substances as the organic dyestuffs is at the present time, with few exceptions, merely a matter of comparison with types. In the case of indigo, which may be regarded as the most important individual dyestuff, it is true that several methods have been carefully worked out and brought to a state of great perfection, by means of which the quantity of colouring matter (indigotine) can be accurately determined either by direct weighing or by means of a quantitative change, such as is brought about by oxidation or reduction. A simple gravimetric process is used in the works for alizarin, and a quantitative method also exists for the estimation of naphthol yellow, picric acid, and the azo dyes based upon their property of forming insoluble molecular compounds with Night blue (Rawson, *Journal of the Society of Dyers and Colourists*, 1888, p. 82). This method of analysis has, however, only found general application in the case of Naphthol yellow S., and for the valuation of this dyestuff it would appear to be the standard one. In almost every other case the chemist, as well as the dyer and printer, relies on colorimetric tests, which are carried out either by means of a specially devised form of apparatus (colorimeter), in which the depths of shade produced by dissolving equal amounts of the samples under examination in water can be gauged, or by the more practical method of making comparative dye-trials. This latter method may be said to have stood the test of time, and is undoubtedly the one on which all makers as well users of organic dyestuffs at present rely. The great advantages of the method are that it indicates directly the following important points :—

(1) The quality or purity of the shade; since in many cases, especially in blues, the value of the dyestuff depends largely upon this point, the operation should never be omitted.

(2) Where samples of the same dyestuff are under examination, the intensity of shade produced in dyeing with a given quantity is a direct indication of the tinctorial value, providing always that the experiment is carried out with an expert knowledge of the best mode of application, and the amount of dyestuff employed gives the most suitable strength of shade for comparison. The various precautions which must be strictly observed in carrying out such comparative dye-trials are well known to those chemists and colourists who have practical experience in the matter.

But after all is said and done, the method of comparison with types either by colorimetry or dye-trials is anything but an absolute one. It affords a means of ascertaining the comparative values of two or more samples of a dyestuff, which to a practised eye will as a rule come within 5 per cent., and in exceptional cases within 2 per cent. of the actual ones. Compared with ordinary analytical methods this cannot, however, be regarded as an exact valuation. Besides, the time required in matching by comparative dye-trials, especially where it is necessary to make exhausts, is excessive. More rapid, though not much more exact, estimations can be obtained by means of a good colorimeter, but if the shades are not an exact match, comparison is rendered more difficult and the results are consequently less certain.

Most dyestuffs (the exceptions belonging mainly to the mordant dyes) are decolourised by the action of strong reducing agents. This phenomenon may be due either to the formation of so-called leuco compounds, as is the case with the basic colours, and their sulphonic acids (where such exist), indophenol, the phthaleïnes, etc., in which cases the original colour can be restored by exposure to air or by means of a mild oxidising agent; or the decolourisation may be due to a permanent change, as is the case with the azo dyes and the nitro-compounds in acid solution. A quantitative method based upon the first of these reactions is that of A. Müller, for the volumetric estimation of indigotine by means of hydrosulphite of soda, which gives accurate results. For the estimation of other dyes which form leuco compounds, stannous chloride has been suggested, but as far as I am aware no results of any practical value have been obtained by this means. The same reagent is employed somewhat extensively by printers for the reduction of the azo dyes in discharge work, in the qualitative analysis of dyestuffs generally, and, according to O. N. Witt, for the quantitative examination of the azo dyes, or rather of their decomposition products. The reaction of stannous chloride with the azo dyes is not, however, of a quantitative character, for in all cases a large excess of the reagent is necessary for complete decolourisation. Having prepared, some two years ago, a small quantity of titanous chloride ($TiCl_3$) in the laboratory by the action of zinc on the tetrachloride, I was struck by the rapidity with which it completely decolourised the azo dyes, when its action was compared with that of stannous chloride of equivalent strength. It at once occurred to me that this might constitute a means of quantitatively estimating the azo dyes, and experiments were carried out with this end in view. The results were, however, not of a satisfactory character, for although they in some cases appeared to be not far removed from the theoretical, a considerable

amount of uncertainty prevailed, which was chiefly due to the instability of the titanous chloride solution, and in some cases to indistinct end reactions. The work was consequently set aside for a time and was only resumed after I had devised a reliable means of keeping the titanous chloride solution and a rapid and exact means of determining its strength. In the meantime the manufacture of the product by electrolysis was taken in hand, and a plentiful supply became available. But now an unexpected difficulty arose, viz., the means of procuring chemically pure azo dyes for the purpose of putting the method to an accurate test. In text books and manuals, as well as in patent literature, we find constitutional formulæ of the numerous azo dyes given with the utmost confidence, which are in the great majority of cases not based upon analytical data, but are merely arrived at by analogy from their construction. That mis-representations may thus arise through too lavish a generalisation of known reactions has been proved in several cases, the most flagrant being that of Chrysophenine, which was shown by Richard Meyer to be a different compound to that claimed in the patent specifications. More recently Sisley* has shown that the azo dyes contain water of crystallisation when separated from their aqueous solutions, but no account of this important fact is taken in the published descriptions, and it may be definitely stated that in no case does the published formula indicate more than the composition of the effective constituent of the commercial article. But even after repeated recrystallisation there is no criterion in the case of the azo dyes for their purity, there being no simple physical data such as melting point or boiling point to go by. A quantitative estimation of a single constituent or even of all constituents is not of much avail, since in the first place the oxygen is determined by difference, and a product of, say, 99·5 per cent. purity would, taking the admitted experimental errors into account, give the same result as one containing 100 per cent. For this reason I took as my standard for testing the method phenyl azo beta naphthol, a substance first described by Liebermann†, which is easily obtained in the pure state by combining diazobenzene chloride with betanaphthol in alkaline solution and crystallising the product several times from alcohol. The substance, which showed the correct melting point, was dissolved in cold fuming sulphuric acid (20 per cent.), and gave, by titration (direct) with titanous chloride, a result in accordance with theory, viz., 100·2 per cent. in place of 100·00 per cent. In another case the product, sulphonated by heating with concentrated sulphuric acid on the water bath for two hours, gave 99·8 per cent.

As is well known, the azo compounds are all more or less readily acted upon by reducing agents in acid solution, the chromophorous

* Bull. Soc. Chim. de Paris, 1901, p. 862.
† Berl. Ber., vol. 16, p. 2858.

group—N:N—being destroyed and converted into two amido groups, e.g.,

$$C_6H_5N : N.C_{10}H_6OH + 2H_2 =$$

$$C_6H_5NH_2 + C_{10}H_6 \begin{cases} OH \\ NH_2 \end{cases}$$
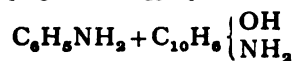
From the hypothetical equation,

$$TiCl_3 + HCl = TiCl_4 + H$$
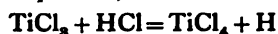
which, of course, only takes place in presence of a reducible substance, it will be seen that each—N:N—group requires 4 TiCl₃ (or 4 Fe) for its complete reduction, and on this the calculations are based.

Storing and Standardising of the Titanous Chloride Solution. The most suitable strength of titanous chloride for titrating I find to be, for general use, a one per cent. solution, obtained by letting down the commercial product with water. For this purpose 50 cc. of the commercial 20 per cent. solution are first mixed with an equal volume of strong hydrochloric acid and boiled for a few minutes in a flask. The solution is then made up to a litre with distilled water which has been previously boiled with the addition of a little hydrochloric acid and a small piece of marble to expel dissolved oxygen. The use of previously boiled water for diluting is not an absolute necessity, but is advisable since it is found the strength of the solution otherwise slowly diminishes subsequently until a certain point is reached and then only becomes constant. With a powerful reducing agent like titanous chloride it is not astonishing that it should rapidly absorb oxygen from the air, and it is therefore absolutely necessary, if reliable results are to be obtained, that it should be stored and measured in vessels in which it is out of contact with the air. A simple arrangement for this purpose is shown in the figure. Sufficient of the reagent is prepared to completely fill the storage vessel S, which is connected with the burette B, both storage vessel and burette being kept under constant hydrogen pressure from the small hydrogen generator G, where the gas is produced from zinc and dilute sulphuric acid. When liquid is withdrawn from the burette at P, the pressure is released and hydrogen is at once generated at G, so that the interior of the apparatus, which is not filled with liquid contains hydrogen at a pressure of about three inches. By this simple means the solution may be kept unchanged for a considerable period. Thus the strength of a solution in use on October 17 was found to be such that 1 cc. = 0·009364 Fe; on October 31st the strength was again determined, when it was found that 1 cc. = 0·009363 Fe. For standardising the titanous chloride solution I employ a standard solution of ferric chloride or ferric

sulphate, having ascertained that the reaction takes place according to the equation :

$$\text{Fe Cl}_3 + \text{Ti Cl}_3 = \text{Fe Cl}_2 + \text{Ti Cl}_4$$
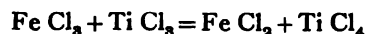
Iron alum may conveniently be employed as the standard ferric salt, but as its purity cannot always be relied on I prefer to use ferrous ammonium sulphate, of which a known quantity is oxidised by nitric acid, the iron precipitated as ferric hydrate with ammonia, and this
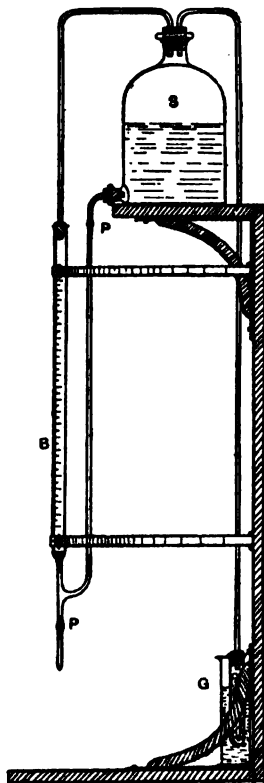
dissolved in hydrochloric acid. Oxidation with permanganate, as suggested to me by one of my former students, Mr. G. T. Yates, is, however, still more convenient, but it should be seen that the permanganate, before being used for this purpose, is free from iron. The following method is the one which I have ultimately adopted : 35 grms. ferrous ammonium sulphate are dissolved in dilute sulphuric acid and made up to one litre; 25 cc. of this solution are now

measured into a flask, and weak permanganate solution run in until a pink colour is just perceptible. Into this solution I now titrate with titanous chloride in the cold, until a drop taken out on a glass rod and spotted on sulphocyanide of potash solution no longer shows a red colouration. When two or more titrations agree, the iron value per cc. of the titanous chloride solution is easily calculated. From what has been said it will be evident that the standardised titanous chloride solution can be employed directly for the volumetric estimation of iron in the ferric condition, and for this purpose I find the method most exact and expeditious. The inverse reaction may serve for the valuation of the commercial titanous salts, but in this case it is necessary to work in an atmosphere of carbonic acid or coal gas.

Estimation of Azo Compounds. Turning now to the actual colour titration, I find here that, according as the azo dye is soluble or insoluble in dilute mineral acid, it is advisable to use one of two methods. With such dyestuffs as are soluble a direct titration can be carried out in the course of a few minutes, the colouring matter acting as its own indicator. For the titrations I find it best to make up a solution of $0·5$ grm. of the dyestuff in 500 cc. distilled water, and take 100 cc. of this. The following example may serve as an illustration :—

Crystal Scarlet 6R. $C_{20}H_{12}N_2S_2O_2Na_2 + 7H_2O$ (colouring matter from alpha naphthylamine and G. salt). $0·5$ grm. of the dyestuff was dissolved in distilled water and the solution made up to 500 cc. Of this, 100 cc. were measured out into a conical flask, and after adding about 10 cc. conc. hydrochloric acid, boiled for about a minute. This amount required $22·6$ cc. of titanous chloride solution.

The calculation is as follows :—

$$1 \text{ cc. } TiCl_3 = 0·0015797 \text{ grm. Fe}$$

and 502 grms. colour require by theory 224 grms. Fe

$$\therefore \frac{0·0015797 \times 22·6 \times 502}{224} = 0·08001 \text{ grm. colour}$$

		Calc.
and 1 gr. contains 0·8001 or	80·01%	20·04
Water of cryst. at 140°C. =	19·96	79·96
Total......	99·97	100·00

Orange II. $C_{16}H_{11}N_2SO_4Na + 5_2H_2O$ (colouring matter from sulphanilic acid and beta naphthol) gave

		Calc.
Colouring matter	79·49%	79·55%
Water of cryst.	20·42	20·45
	99·91	100·00

Cotton Scarlet. $C_{22}H_{14}N_4S_2O_2K_2 + 2H_2O$ (potassium salt of the colouring matter from amidoazobenzene and R. salt) gave

		Calc.
Colouring matter............	94·29%	94·24%
Water of cryst.	5·83	5·76
	100·12	100·00

In the case of dyestuffs which, like the majority of the benzidine derivatives, are thrown out of solution by hydrochloric acid, the reaction is too slow and the end of the reaction often not sufficiently sharp to admit of exact estimations. In such cases I find it best to run in an excess of titanous chloride solution into the boiling solution of the dyestuff, taking the precaution to keep a gentle current of carbonic acid (from a Kipp, or better still, a Kekulé generator) passing into the flask by a tube which almost touches the surface of the liquid. The reduction will usually be completed in less than two minutes, when the flask is cooled under the tap, without, however, interrupting the current of carbonic acid. When cold, the excess of titanous chloride is estimated as already described by running in iron alum solution of known strength (but preferably nearly equivalent to that of the titanous chloride solution) until a drop taken out and spotted on sulphocyanide of potash solution just shows a red colour. By subtracting the number of ccs. of the iron alum solution (or their equivalent in titanous chloride, should the two solutions not be of equal strength) from the total number of ccs. of titanous chloride run in, the exact amount of the latter used up in the reduction of the dyestuff is arrived at. The method tested with the chemically pure potassium salt of Benzopurpurin 4B gave the following result :—

Benzopurpurin 4B, $C_{34}H_{26}N_6S_2O_6K_2 + 4\frac{1}{2} H_2O$ (potassium salt of the colouring matter from tolidine and naphthionic acid. The potassium salt of this dyestuff was chosen in preference to the sodium salt on account of the difficulty experienced in obtaining the latter in a chemically pure state. It was prepared in the laboratory from materials free from sodium and crystallised twice from dilute a'cohol. The microscopic needles thus obtained undergo a remarkable change when heated under pressure with alcohol for about ten minutes, being converted into rhombic plates, showing a metallic reflex). 0·5 grm. of the dyestuff is dissolved in distilled water, and the solution made up to 500 cc. Of this 100 cc. were measured into a conical flask and heated to the boil. 10 cc. conc. hydrochloric acid and 50 cc. titanous chloride solution were then added, carbonic acid being passed into the flask. The contents of the flask were now boiled for about a minute, when complete reduction took place, and, after cooling, the solution required 22·9 cc. iron alum (equivalent to

21'0 cc. titanous chloride). The excess of titanous chloride added was therefore 21'0 cc., and this, subtracted from 50, gives 29'0 cc. titanous chloride as having been used for the reduction. The calculation is as follows :—

$$1 \text{ cc. TiCl}_3 = 0\text{'}001845 \text{ grm. Fe}$$

and 756 grms. colour require by theory 448 grms. Fe

$$\therefore \frac{0\text{'}001845 \times 29 \times 756}{448} = 0\text{'}09026 \text{ grm. colour.}$$

		Calc.
and 1 grm. contains 0'9026 or	90'26%	90'33%
Water of cryst.	9'63	9'67
	99'89	100'00

Brilliant Yellow. $C_{26}H_{18}N_4S_2O_8Na_2 + 3H_2O$ (Colouring matter from diamidostilbene disulphonic acid and phenol) gave—

		Calc.
Colouring matter	91'90%	92'02%
Water of cryst.	8'00	7'98
	99'90	100'00

Estimation of Nitro-compounds. As with the azo dyes, I have ascertained that the reduction by means of titanous chloride takes place quantitatively, the nitro groups being reduced to the corresponding amido groups. According to the scheme

$$-NO_2 + 3H_2 = \quad -NH_2 + 2H_2O$$
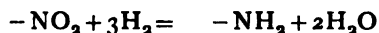
each nitro group requires six molecules of titanous chloride for its complete reduction. Although many of the nitro-compounds are intensely coloured, they cannot act as their own indicators, since the colour vanishes before the end of the reaction is reached. Consequently the indirect method as described for benzopurpurin must be employed for their estimation. The amount of substance used in the titration will necessarily be smaller than in the case of a simple azo dye. Where more than one nitro group is present, naturally more reducing agent is required, and the amount of substance taken for a titration must be chosen accordingly.

Nitrobenzene. A known weight of this substance (m.p. 7°C.) was sulphonated by heating with about twenty times its weight of fuming suphuric acid (20 per cent.) on a water bath for two hours. It was then titrated by the indirect method, and the following results were obtained :—

Calculated 100. Found, I., 99'98; II., 99'60.

A freshly distilled commercial sample gave 99'75%.

Picric Acid. This product was purified by repeated crystallisation, and showed the correct melting point (m.p. 122·5). It was dried at 100° before weighing. The analyses yielded the following figures—

Calculated 100. I., 100·13; II., 100·16.

Paranitraniline. This product was crystallised several times from alcohol, and showed the melting point 147°. It was dried at 100° before weighing. Like the preceding two, it was titrated by the indirect method. The results were

Calculated 100. I., 99·92; II., 99·68.

A commercial product gave 99·0. From the following result the process would also appear to be suitable for nitroso compounds :—

Nitrosodimethylaniline (m.p. 85°), purified by recrystallisation from carbon tetrachloride, can be estimated by the direct method, the intense yellow colour with which it dissolves in water acting as indicator. The only precaution to be taken is that during tne titration the solution should be warmed to 40-50°C. The result was—

Calculated 100. Found 99·88.

For pure materials the process seems to be an absolute one, and comparison with types for ascertaining strength is thereby rendered unnecessary, unless added impurities or bye-products formed in the process of manufacture were found to exert an oxidising action on the titanous chloride. So far, however, I have not been able to detect such. The only impurity sometimes occurring in the azo dyes which is likely to affect the results is ferric iron. In case this is present in such quantity as to be likely to influence the result, it could be estimated in the ash by the method indicated above. The apparatus necessary for carrying out the estimations is neither costly nor complicated, and as the method is capable of giving exact results and has the additional advantage of being a rapid one, I hope that it will be of service to some members of this society.

From preliminary experiments which I have carried out with certain classes of dyestuffs which are reduced by titanous chloride to colourless leuco compounds, it would appear probable that the process would also render good service. Further investigation with chemically pure materials will prove or disprove this, and in case the results should warrant it, I shall be pleased to bring to your notice a further communication on the subject. I may state here that in the case of the disulphonic acid of indigotine, the reduction is apparently quantitative when the blue colour disappears, but the change is only sharp when certain specific conditions are observed. Indirubine sulphonic acid is similarly acted upon. It is my intention to further investigate the behaviour of these two substances with a view to substituting, in Müller's process for the valuation of indigo,

titanous chloride for the unstable hydrosulphite. The same would apply to the estimation of dissolved oxygen in water. The future uses of titanous chloride as a reagent in volumetric analysis may possibly be far more numerous than can at present be predicted. So far (apart from alkalimetry and acidimetry) oxidising agents have played the most important rôle in this branch of analytical chemistry. A powerful acid reducing agent which can be kept in an unchanged condition for a reasonable period has been wanting. Such a one is now readily accessible, and I have no doubt will find application.

Method for the Volumetric Estimation of Indigo, some Basic Colours & Eosins.

By Professor EDMUND KNECHT, Ph.D., F.I.C.

I N the foregoing papers I have described a volumetric method for the estimation of azo-dyes, picric acid and other nitro compounds, which was based upon the reducing action of titanous chloride in hydrochloric acid solution. I have also described a method for the quantitative estimation of Methylene Blue, and intimated that I had succeeded in applying the method in the case of Paraosaniline.

In all these processes the end of the reaction is marked by a disappearance of the colour, which acts, in the majority of cases, as its own indicator. It will be noted that this decolourisation is due to different causes, according to the chemical constitution of the colouring matter. Thus, in the case of Naphthol Yellow S, which we may regard as a type of the nitro-colouring matters, it is the result of the reduction of the chromophorous nitro groups to the colourless (in-effective) amido groups; with Crystal Scarlet, as a type of the azo-dyes, to the destruction of the azo group, with simultaneous dismemberment of the molecule; while with such colouring matters as Methylene Blue, which are known to yield colourless leuco compounds, the reaction is again different, inasmuch as the original dyestuff can be readily regenerated, either by exposure to the air or by means of an oxidising agent. For these three classes of dyestuffs the amounts of reducing agent required to bring about decolourisation vary considerably. Thus, in the case of the nitro dyestuffs, an amount equivalent to six hydrogen atoms is required for each nitro group present in the molecule, while for each azo group in the azo-dyes, the amount required is equivalent to 4H. For the dyestuffs which yield colourless leuco compounds, much less reducing agent is required than for the preceding classes, the amount being as a rule equivalent to 2H for the whole molecule. With dyestuffs, such as Indoine, Anthracene Red, and Methylene Green, which each contain two different chromophores, the amount varies accordingly. In the present paper I propose to deal exclusively with the volumetric estimation of colouring matters of the third type, viz., those which yield colourless leuco compounds. The *modus operandi* does not differ from that which I originally suggested, the titration being generally effected at an elevated temperature, and in a current of deoxidised coal-gas, or of carbon dioxide.

Indigo. I have previously pointed out that when pure indigotin is employed, the reduction by $TiCl_3$ in tartaric acid solution gives an absolutely sharp end reaction, and is quantitative. With medium and low grade Indigoes, however, the end of the reaction was found

to be so marked by the impurities present that we considered the method to be of no value for commercial analyses. In a paper read before the Society of Chemical Industry, in March, 1905, Dr. Grossman showed, however, that after sulphonation the impurities in natural Indigoes are insoluble in neutral solution, and he effected their removal by an extremely simple device, viz., by the addition of an excess of chalk.* By adopting Grossman's modification, all difficulties were removed, and even in the case of low grade Indigoes absolutely sharp end reactions were obtained. The modified method was tested on a sample of (chemically) pure indigotin, for which I am indebted to the Badische Anilin und Soda Fabrik, and which yielded, according to their analysis, 99.5 per cent. of indigotin. One gramme of this product was sulphonated with 5 cc. strong sulphuric acid. The solution thus obtained was poured into water and made up to 500 cc. Of this 50 cc. were transferred, along with 25 cc. of a 20 per cent. Rochelle salt solution, to a conical flask, provided with an indiarubber stopper having three holes, one for the introduction of the carbon dioxide, a second for the escape of the gas, and the third for the tube attached to the $TiCl_3$ burette. The Indigo solution was first heated to the boil, and after the air had been displaced by carbon dioxide, the titanous chloride run in until the blue colour changed to yellow.

$$1 \text{ cc. } TiCl_3 = 0.001557 \text{ grm. Fe.}$$

Required for titration 27.3 cc. $TiCl_3 = 0.04251$ Fe., and since 112 Fe. = 262 indigotin, we have—

$$\left. \frac{0.04251 \times 262}{112} \right\} = 0.09943 \text{ or } 99.43\%$$

In the following examples the sulphonating was effected as described above, the Indigo solution diluted to about 300 cc., and poured into a 500 cc. graduated flask. Twelve grms. of chalk were then added to the warmed solution, and after evolution of CO_2 had ceased, the contents were made up to 500 cc. When the precipitate had settled (this takes place in 20-30 min.), 50 cc. of the clear solution were drawn off, and titrated as above in presence of Rochelle Salt. In making the calculation, an allowance must be made for the $CaSO_4$ and $CaCO_3$, the actual amount of Indigo solution being 499 cc. instead of 500 cc. This figure was determined experimentally.

Indigo.	By. $TiCl_3$.	By. $KMnO_4$ (Rawson).	Gravimetrically[†] (Möhlau and Zimmermann).
Bengal I.	59.08%	59.14%	58.5%
Bengal II.	55.97%	56.00%	57.0%
Kurpah	35.32%	—	30.0%
Fig.	32.61%	32.47%	33.5%

* Journal of the Society of Dyers and Colourists, 1905, p. 171.
† „ „ „ „ „ 1903, p. 206.

THE ESTIMATION OF INDIGO, &c.

Both indigotin and indirubin are reduced by $TiCl_3$. The titration by $TiCl_3$ is more rapid than the gravimetric estimation, and the end reaction is sharper than with permanganate. With artificial Indigoes, which contain the red substance mentioned in their paper by Möhlau and Zimmermann, the results are too high, since the red substance also yields a leuco compound. In the more recent artificial products, however, this red substance is not present in anything like the quantities stated by Möhlau and Zimmermann, and in some of our samples it was absent altogether. I do not claim that the process has any material advantages over the permanganate process, and it is consequently not likely that it will take its place for ordinary purposes. But where oxidisable substances are present which would act on the permanganate and cannot be got rid of, the method might be of good service.

Pararosaniline Hydrochloride. The hydrochloride used for the experiments was prepared from chemically pure rosaniline, and was purified by recrystallisation from water. A nitrogen determination gave the following result :—

Found ... ... $N = 10.78\%$
Calculated for $C_{19}H_{18}N_3Cl + 4H_2O = 10.62$

For the analysis one gramme of the dyestuff was dissolved in water, and the solution made up to 500 cc. Of this solution 50 cc. were taken, and after adding 25 cc. of a 20 per cent. Rochelle salt solution, heated to the boil, and then titrated in a current of CO_2.

1 cc. $TiCl_3 = 0.001622$ grms. Fe.

Required 17.35 cc. $TiCl_3$, and as 112 Fe. $= 323.5$ Pararosaniline hydrochloride, we get

Dyestuff ... ... $= 81.28\%$
Water of cryst. ... ... $= 18.60$

————
99.88

Calc. for $C_{19}H_{18}N_3Cl + 4H_2O = 18.20\%$.

Pararosaniline Trisulphonic Acid. This product, which would correspond to Acid Magenta, was not actually isolated as such, but was prepared by the sulphonation of a known weight of the Pararosaniline hydrochloride quoted in the previous example. Of this, one gramme was sulphonated with fuming sulphuric acid at 30° to 40°C., the solution thus obtained being poured into water and made up to 500 cc. The titration was effected in exactly the same way as described for the unsulphonated product, and gave 81.38 per cent. dyestuff (against 81.28 per cent. found in the unsulphonated dye-stuff—see above).

Crystal Violet. This dyestuff, which represents the hydrochloride of hexamethylpararosaniline, was easily obtained in the pure state by recrystallising the commercial product from water. A nitrogen determination gave the following result :—

Found   ...   .   N = 7·22%
Calc. for $C_{25}H_{30}N_3Cl + 9H_2O$ ...   N = 7·37%

The titration of the dyestuff was effected in exactly the same way as in the case of Pararosaniline hydrochloride.

Dyestuff found   ...   .   71·67%
Water of cryst.   ...   .   28·45%
                                          ————
                                          100·12%

Calc. for $C_{25}H_{30}N_3Cl + 9H_2O$.   28·44.

Malachite Green. The dyestuff, which consists of the oxalate of tetramethyldiamidotriphenyl carbinol, was purified by recrystallisation from water. A nitrogen determination gave the following result :—

Found   ...   .   N = 6·04%
Calc. for $2C_{23}H_{24}N_2 + 3C_2H_2O_4 + 2H_2O$....   N = 5·85%

The same mode of procedure was adopted in titrating as in the preceding cases, but it was found that the product behaved in a somewhat different manner towards the reducing agent, inasmuch as decolourisation of the solution ensued after the addition of 3-4 cc. The colour returned, however, after a few seconds, vanishing again with the next addition of $TiCl_3$, but again returning, until, when the reduction is complete, this phenomenon ceases. (Possibly this temporary decolourisation is due to the free hydrochloric acid contained in the $TiCl_3$.) For the titration, one gramme of the dyestuff was dissolved in water and the solution made up to 500 cc. Of this solution, 50 cc. were taken, mixed with 25 cc. Rochelle salt solution, heated, and titrated in a current of CO_2.

1 cc. $TiCl_3$ = 0·001612 grm. Fe.

Required 29·0 cc. $TiCl_3$, and since 224 Fe = 926 Malachite Green, we have

Dyestuff   ...   .   96·55%
Water of cryst.   ...   .   3·40%
                                          ————
                                          99·95%

Calc. for $2C_{23}H_{24}N_2 + 3C_2H_2O_4 + 2H_2O$.   3·70%.

Another sample, previously dried at 100°, gave 99·71 per cent. colour.

Tolusafranine. The dyestuff which served for this estimation was a beautifully crystallised specimen, for which I am indebted to Dr. T. Sandmeyer. A nitrogen determination yielded the following result :—

Found ... ... $N = 13·05\%$
Calc. for $C_{21}H_{21}N_4Cl + 3\frac{1}{2}H_2O.$ ... ... $N = 13·09\%$

The quantitative reduction of Phenosafranine was first effected by Nietzki[*] by means of stannous chloride, but no definite figures are given. In working by the same process that I used for the preceding dyestuffs, I constantly obtained figures which were considerably in excess of the theoretical ones (7-8 per cent. above). These results led me to suspect that the sample I was experimenting with was a Phenosafranine, for which the volumetric results agreed very closely. Being assured, however, by Dr. Sandmeyer that the product he had sent was Tolusafranine, and this was borne out by the percentage of nitrogen found and the appearance of the crystals, I felt inclined to relinquish the work. At this point it occurred to me, however, that by the use of so large an excess of Rochelle salt, we were effecting the reduction in alkaline solution and that possibly the reaction was not normal under such conditions. This appears to have been the case, for by substituting bitartrate of soda[†] for the Rochelle salt, results were obtained which closely approximated to the theoretical value. For the titration, one gramme of Tolusafranine was dissolved in water and the solution made up to 250 cc. Of this solution 25 cc. were measured into a flask along with 25 cc. of a saturated solution of bitartrate of soda, the titration being effected as usual.

1 cc. $TiCl_3 = 0·001557$ grm. Fe.

Required 17·05 cc. $TiCl_3$, and since 364·5 Tolusafranine $= 112$ Fe, we have

Dyestuff ... ... 86·39%
Water of cryst. ... ... 13·80%
———
100·19%

Calc. for $C_{21}H_{21}N_4Cl + 3\frac{1}{2}H_2O.$ 14·77%.

Indoïne. The titration of this blue dyestuff, which is obtained by combining diazotised Tolusafranine with β naphthol, is of special interest, since it contains two chromophors. Of these, the azo group is destroyed first, with regeneration of the Safranine, and by further addition of $TiCl_3$, this is decolourised. I am also indebted to

[*] *Chem. der künstl. Farbst.*, 4th ed., p. 226.

[†] This salt can also be used with advantage in the other titrations, for when Rochelle salt is brought into contact with mineral acids, as is the case in some of the titrations (indigo, acid magenta, &c.), the separation of tartar is sometimes so copious that it interferes with the accuracy of the process.

Dr. T. Sandmeyer for the crystallised sample which served for the analysis. A nitrogen determination gave :—

$$N = 12\cdot28\%$$
Calc. for $C_{31}H_{27}N_5OCl + 3\tfrac{1}{2}H_2O$. $N = 12\cdot00\%$

The titration was effected as in the case of Tolusafranine.

Dyestuff	89·42%
Water of cryst.	10·30%
	99·72%

Calc. for $C_{31}H_{27}N_5OCl + 3\tfrac{1}{2}H_2O$.   10·80%.

Eosin A. As is well known, the dyestuffs belonging to this group are not easily reduced, especially in acid solution. By heating a solution of Eosin or Rhodamine in presence of Rochelle salt with $TiCl_3$, decolourisation ensues after a time, but the solution becomes turbid, owing probably to the separation of the leuco compound, and the end reaction is in consequence not clear. But by adding an equal volume of alcohol to the solution previous to running in the reducing agent a perfectly distinct and sharp end reaction was obtained. The Eosin used for analysis was the sodium salt of tetrabromfluorescein, which was obtained in beautiful red crystals from the solution in dilute alcohol. A sodium estimation (as Na_2SO_4) gave :

$$Na = 5\cdot39\%$$
Calc. for $C_{20}H_6O_5Br_4Na_2 + 10H_2O$.   5·29%

One gramme of the dyestuff was dissolved in water, the solution made up to 250 cc., and of this 50 cc. were taken, mixed with 25 cc. of a 20 per cent. solution of Rochelle salt and 50 cc. alcohol. The titration was effected as usual.

1 cc. $TiCl_3 = 0\cdot001660$ grm. Fe.

Required 15·5 cc. $TiCl_3$, and since 689·6 Eosin = 112 Fe, we have

Dyestuff	79·21%
Water of cryst.	20·50%
	99·71%

Calc. for $10H_2O$.   20·70%

Rhodamine B. The base which served for the analysis formed beautiful red cubical crystals, with a metallic reflex. A nitrogen estimation gave :—

$$N = 5\cdot16\%$$
Calc. for $C_{28}H_{31}N_2O_3 + 4H_2O$ $N = 5\cdot45\%$

For the titration one gramme of the base was dissolved in tartaric acid, the solution made up to 250 cc., and of this 50 cc. titrated as in the case of Eosin A.

$$1 \text{ cc. } TiCl_3 = 0.001645 \text{ grm. Fe.}$$

Required 26·95 cc. $TiCl_3$, and since 443 of the base = 112 Fe, we have

Dyestuff	86·87%
Water of cryst.	13·20% ·

	100·07%
Calc. for $4H_2O$.	13·90%

Spirit Blue. Two well-crystallised samples of Spirit Blue which had been prepared in the works gave, after sulphonating and titrating (as with Indigo), results which were far from encouraging (107 and 90 per cent. respectively). Two other samples, which we prepared ourselves in the laboratory from chemically pure Para-rosaniline, yielded by the same treatment almost theoretical results, and were found to contain nitrogen equivalent to the amount contained in triphenylrosaniline. In view, however, of the statement of Baeyer and Villiger* that commercial Aniline Blue consists almost entirely of diphenylrosaniline, I prefer to go further into the matter before giving definite figures. What applies to Spirit Blue naturally also applies to the technically far more important Alkali Blues and Soluble Blues. So far, I have not found it possible to reduce Auramine by $TiCl_3$, and the same naturally applies to Thioflavine T, so that for these dyestuffs the method is not available. It is probable, however, that it will be found to give satisfactory results with dyestuffs other than those enunciated, which yield colourless leuco compounds. We have recently observed that Haematein is easily reduced to a colourless compound by $TiCl_3$, but have not yet been able to follow the reaction quantitatively. The examples quoted in this paper show that the reduction method is applicable to the most important of the basic dyestuffs and yields results which, for accuracy, cannot be approached by any other method. If the titanium solution is made up and standardised, such estimations can be easily conducted in 20-30 minutes, so that in point of time the method also has the advantage over others.

* *Berl. Ber.*, 1904, p. 2870.

The Estimation of Methylene Blue

By Professor EDMUND KNECHT, Ph.D., F.I.C.

IN the *Bulletin de la Société Chimique de Paris*, 1904, p. 1094 (see p. 18, vol. 21 of the *Journal of the Society of Dyers and Colourists*), an article is published by L. Pelet and V. Garuti on the volumetric estimation of Methylene blue, which is based upon the observation that this dyestuff yields insoluble precipitates with various azo dyes. The method adopted is to run into a solution of Methylene blue of known strength a standard solution of Crystal scarlet (1 grm. per litre) until a drop of the liquid spotted on filter paper shows a red halo. I have tried similar processes before, with the intention of utilising the interaction of acid and basic dyestuffs for the estimation of one of them, but came to the conclusion that no accurate results could be thereby attained. Indeed, it stands to reason that in using solutions of the strength indicated by these authors it would not be possible to distinguish between a dyestuff containing 98 per cent. from one containing 99 per cent. of Methylene blue, as this would mean being able to see distinctly in such a thin layer as is produced on filter paper one part of Crystal scarlet in about 100,000 parts of water. The method can therefore scarcely be called a quantitative one, but it appears nevertheless to have aroused a considerable amount of interest as something new and original. It is surprising to find that no reference is made in the paper to the original method based on these lines first devised by Ch. Rawson* for the quantitative estimation of Naphthol Yellow S, which was first published sixteen years ago in the *Journal of the Society of Dyers and Colourists†* and subsequently in the *Chemiker Zeitung,‡* and in *A Manual of Dyeing,§* as well as in the German edition,‖ and which has not only been generally adopted for the purpose for which it was originally intended, but may also be used for picric acid,¶ and, as indicated by Rawson,** for azo dyes. In Rawson's original paper it was pointed out that the liquid must be filtered into a Nessler glass in order to render the colour of the Naphthol yellow visible, and thus render accurate results possible. I know that he had tried spotting on filter paper (although this is not mentioned in his paper), and that he soon concluded that this was of no use for obtaining a sufficiently sharp indication of the end reaction. I have recently found that accurate results can be obtained in the case of Methylene blue by utilising the well-known fact that it is decolourised by reducing agents. Since this dyestuff is not appreciably affected by hydrochloric acid, it appeared to me that titration with titanous chloride to decolourisation would

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*Mention is made of Rawson's method of estimating *Night blue*, but it is evident from this that the authors can neither have read the article in the original nor in the publication quoted in the footnotes.

† 1888, p. 82.   ‡ 1888. No. 52.   § p. 826.   ‖ *Handbuch der Färberei*, 1900, p. 1433.

¶ *The Journal of the Society of Dyers and Colourists*, 1888, p. 83.   ** l.c.

yield accurate results. A rough trial showed that the end reaction was sharp and unmistakable. A sample of medicinal Methylene blue which I obtained from a large firm of colour makers as chemically pure, yielded the following results, which are based on the assumption that Methylene blue with the constitution ascribed to it by Bernthsen requires two equivalents of hydrogen for its conversion into the leuco compound, according to the equation.

$$C_{16}H_{18}N_3SCl + H_2 = C_{16}H_{20}N_3SCl.$$

One gramme of the pure product was dissolved in 250 cc. water, 50 cc. of the solution were measured into a conical flask, a few drops of hydrochloric acid added and the contents of the flask gently warmed over a Bunsen. Carbonic acid was now passed into the flask and titanous chloride solution run in until the blue colour just disappeared. The amount found in this way was 78'70 per cent. To this must be added the water contained in the air-dried product, which amounted to 20'4 per cent., making a total of 99'1 per cent. This result was not quite so satisfactory as some of those which I had previously obtained with azo dyes. I consequently asked Messrs. Claus and Rée whether they could supply me with a still purer article. They kindly supplied me with a small quantity of the dyestuff, which had been specially purified by recrystallisation from alcohol, and which gave on analysis the following figures :—

Moisture	4'00%
Colouring matter	95'96%
	99'96%

The method of carrying out the assay of commercial Methylene blue scarcely calls for any further explanation. One gramme of the sample is dissolved in 250 cc. water and 50 cc. of this are titrated as indicated. If the standard solutions are ready for use, a single estimation (two titrations) can easily be performed in twenty minutes. Of other basic dyes I have so far only tried a crystallised sample of Safranine, which I take to be Phenosafranine, but the result did not agree with the formula of the latter.

On Convective Equilibrium of a

spherical mass of gas subject only to the mutual gravitation of its parts.

By Mr. J. PRESCOTT, M.A.

BEFORE attacking the question from a mathematical standpoint, let us get some idea from physical considerations how the radius of the sphere of zero density depends on the mass of the gas. Suppose that, when a mass of gas acted on by no forces except its own gravitation has taken up its equilibrium state, it were possible suddenly to double its density at every point by placing in every portion of space an exactly equal and similar mass of gas to that which already occupies the space. The pressure would be doubled everywhere, and therefore the resultant of the pressures acting on the gas enclosed within any given space would be doubled. But the mass within the space would be doubled, and the attracting mass likewise doubled; hence the resultant attraction would be quadrupled. And since, before the alteration in density, the pressures and attraction balanced, it follows that the attraction under the new conditions would be preponderant everywhere and each element would move nearer the centre of the sphere. Thus the larger mass, starting from the same initial conditions as the smaller mass, will occupy the smaller volume. In the preceding argument there is no assumption concerning the variation of temperature throughout the mass; and therefore the conclusion is true however the temperature may vary from point to point. The consideration that the smaller the mass the larger is the sphere occupied by a gas led me to suspect that there might be a critical mass of gas which, starting with a given amount of internal energy per unit mass, would just diffuse to infinity. In the case of convective equilibrium, however, I find that this surmise is not correct. Although the bounding sphere may become very great for small masses, yet it never becomes infinite. But practically a small mass of gas could not be held together by its own gravitation in the neighbourhood of other bodies; for the attraction on the outer portions of the mass would be so small that the slightest attraction, even from distant external bodies, would suck some of it away, and this process would go on until nothing was left. Now I propose to obtain the relation between the density ρ and the distance from the centre r in a mass of gas in convective equilibrium. The equation expressing the condition of equilibrium is

$$\frac{dp}{dr} = -\rho F, \qquad \qquad \qquad (1)$$

where p is the pressure, and F is the attraction on unit mass at a distance r.

Thus

$$F = \frac{K}{r^2} \int_0^r \rho 4\pi r^2 dr, \quad \cdots \cdots \quad (2)$$

K being the constant of gravitation.

Hence

$$\frac{dp}{dr} = -\frac{K\rho}{r^2} \int_0^r 4\pi \rho r^2 dr. \quad \cdots \cdots \quad (3)$$

Assuming convective equilibrium we have

$$p = c\rho^\gamma.$$

The equation of equilibrium now becomes

$$c\gamma\rho^{\gamma-1}\frac{d\rho}{dr} = -\frac{K\rho}{r^2}\int_0^r 4\pi\rho r^2 dr, \quad \cdots \quad (4)$$

or

$$c\gamma\frac{r^2}{\gamma-1}\cdot\frac{d(\rho^{\gamma-1})}{dr} = -4\pi K\int_0^r \rho r^2 dr, \quad \cdots \quad (5)$$

By means of the substitutions

$$\rho^{\gamma-1} = y$$

$$\frac{1}{r} = z,$$

this last equation reduces to

$$\frac{dy}{dz} = -\frac{4\pi K(\gamma-1)}{c\gamma}\int_\infty^z y^{\frac{1}{\gamma-1}}\frac{1}{z^4}dz. \quad \cdots \quad (6)$$

Now putting, for convenience,

$$x = z \cdot \sqrt{\frac{c\gamma}{4\pi K(\gamma-1)}},$$

and differentiating with respect to the upper limit, we get

$$\frac{d^2y}{dx^2} = -\frac{y^{\frac{1}{\gamma-1}}}{x^4}. \quad \cdots \cdots \quad (7)$$

Being unable to find the general solution of this equation I have concentrated my attention on a single solution of the type which applies to the physical problem, and I shall shortly show that this single solution can be adapted to any mass of gas.

Let us take $\gamma = 1\cdot4$. If we start with $y = 0$ when $\frac{dy}{dx} = m$ and $x = a$, m and a being both positive, then so long as the curve for x and y does not cross the axis of x again we know that $y < mx$; consequently

$$-\frac{d^2y}{dx^2} < \frac{m^{2\cdot5}x^{2\cdot5}}{x^4};$$

therefore

$$m - \frac{dy}{dx} < \int_a^x \frac{m^{2\cdot5}}{x^{1\cdot5}}dx.$$

The right hand side of this inequality is finite when the upper limit is infinite. Hence, if we start with suitable values of m and a, the value of $\frac{dy}{dx}$ will approach some constant as x becomes infinite; *i.e.* the curve will have an asymptote. The only types of curve which will apply to the physical problem are those to which this asymptote is parallel to the axis of x and at a finite distance from it; for the value of y when x is infinite is the value of $\rho^{\gamma-1}$ at the centre of the sphere. It is easier to start with x infinite and $\frac{dy}{dx}$ zero and work towards the origin. I therefore began with $y = 100$, $\frac{dy}{dx} = 0$ when $x = \infty$, and proceeded by successive steps until y became zero. The values obtained are only approximate ones, but I do not think the errors in the values of x and $\frac{dy}{dx}$ when y is zero are greater than 5 or 6 per cent. The following table gives the calculated values of $\frac{dy}{dx}$ and y.

x.	$\frac{dy}{dx}$.	y.	x.	$\frac{dy}{dx}$.	y.
∞	0	100	21	2·347	72·07
100	·0333	98·33	20	2·588	69·60
80	·0525	97·47	19	2·856	66·88
60	·0993	95·95	18	3·154	63·87
50	·1689	94·61	17	3·483	60·55
40	·3045	92·25	16	3·844	56·89
36	·5321	90·78	15	4·232	52·85
32	·8796	88·28	14	4·649	48·40
30	1·051	86·38	13	5·085	43·54
29	1·141	85·29	12	5·529	38·23
28	1·241	84·10	11	5·960	32·49
27	1·352	82·81	10	6·352	26·34
26	1·475	81·41	9	6·670	19·83
25	1·613	79·87	8	6·877	13·06
24	1·767	78·18	7	6·957	6·14
23	1·939	76·33	6·10	6·98	0
22	2·131	74·30			

The accompanying curve shows the relation between y and x from the point where $y = 0$ to $x = 40$. The numbers in the table can easily be converted into distance from the centre and density by means of the relations

$$r = \frac{1}{x} \cdot \sqrt{\frac{c\gamma}{4\pi K(\gamma - 1)}},$$

and

$$\rho = y^{\frac{1}{\gamma - 1}} = y^{2 \cdot 5}.$$

Taking

$$c = 15 \times 144 \times 13^{1 \cdot 4} \times 32 \cdot 2,$$

which is the value, in foot pound units, of $\dfrac{p}{\rho^{1 \cdot 4}}$ in our atmosphere at the surface of the earth ; and taking also

$$K = \frac{1}{9 \cdot 3 \times 10^{8}},$$

we get that

$$r = \frac{1}{x} \times 25 \cdot 5 \times 10^{6} \text{ feet,}$$

$$= \frac{1}{x} \times 4820 \text{ miles.}$$
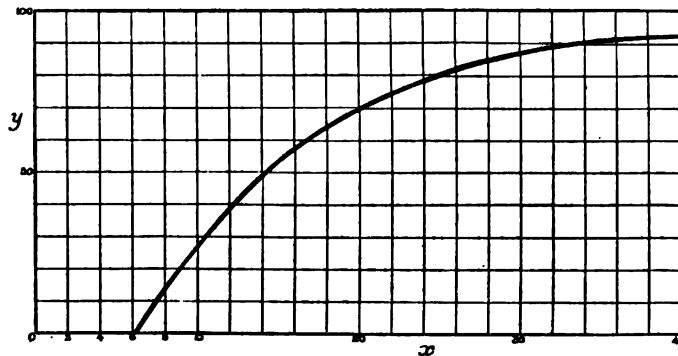
When ρ is zero $r = 790$ miles, and when r is zero $\rho = 100,000$. This, however, does not correspond to any physical conditions, for the density of a gas cannot have such a large value. I shall now show, however, how the solution can be adapted to give any arbitrary value of ρ at the centre. If we put

$$\rho^{\gamma - 1} = py.$$

and

$$r = q\frac{1}{x}\sqrt{\frac{c\gamma}{4\pi K(\gamma - 1)}}$$

in equation (5), p and q being constants, we get

$$pq^2\frac{d^2y}{dx^2} = -p^{2\cdot5}\,q^4\frac{y^{2\cdot5}}{x^4};$$

and if we make $p^{1\cdot5}\,q^2 = 1$, this reduces to equation (7) whose solution has been obtained. Denoting by M the total mass of the sphere, we know that

$$M = 4\pi\int_0^{r_0}\rho r^2\,dr,$$

the subscript $(_0)$ indicating values of quantities when $\rho = 0$. Substituting for ρ and r we get

$$M = 4\pi\left\{\frac{c\gamma}{4\pi K(\gamma-1)}\right\}^{\frac{3}{2}}\int_{x_0}^{\infty}p^{2\cdot5}\,q^3\frac{y^{2\cdot5}}{x^4}\,dx$$

$$= 1\cdot20\times10^{11}\times q^{-\frac{1}{2}}\int_{x_0}^{\infty}\frac{y^{2\cdot5}}{x^4}\,dx$$

$$= 1\cdot20\times10^{11}\times q^{-\frac{1}{2}}\int_{\infty}^{x_0}\frac{d^2y}{dx^2}\,dx$$

$$= 1\cdot20\times10^{11}\times q^{-\frac{1}{2}}\left(\frac{dy}{dx}\right)_0$$

$$= 1\cdot20\times10^{11}\times6\cdot98\times q^{-\frac{1}{2}}.$$

Therefore $\qquad q^{\frac{1}{2}} = 8\cdot4\times10^{11}\times M^{-1}$,

and $\qquad p^{\frac{1}{2}} = q^{-\frac{3}{2}}$

$$= \frac{M}{8\cdot4\times10^{11}}.$$

Hence

$$r = \left(\frac{8\cdot4\times10^{11}}{M}\right)^2\frac{1}{x}\sqrt{\frac{c\gamma}{4\pi K(\gamma-1)}}$$

and $\qquad \rho = (py)^{2\cdot5}$

$$= \left(\frac{M}{8\cdot4\times10^{11}}\right)^{10}y^{2\cdot5}.$$

Thus, by means of the table given, the density at any point can be obtained when the mass is given. Let us find the radius of the sphere whose density at the centre is 10 lbs. per cubic foot. At the centre

$$\rho = 10 = \left(\frac{M}{8\cdot4\times10^{11}}\right)^{10}10^5.$$

Therefore $\qquad \dfrac{8\cdot4\times10^{11}}{M} = 10^{\frac{2}{5}}.$

And at the surface of zero density

$$r = 10^{18} \times \frac{1}{6 \cdot 1} \times 25 \cdot 5 \times 10^6 \text{ feet}$$

$$= 12600 \text{ miles about.}$$

Also if the density at the centre is 1 lb. per cubic foot the radius of the containing sphere is about 25,100 miles. I will now investigate what effect the contraction of the gas has on the temperature. Let us first transform the equation of equilibrium so as to make θ, the temperature, the dependent variable, instead of ρ. We have assumed

$$\frac{p}{\rho^\gamma} = c.$$

But

$$\frac{p}{\rho} = R\theta.$$

Hence

$$c\rho^{\gamma-1} = R\theta.$$

Thus, since

$$c\frac{d(\rho^{\gamma-1})}{dr} = R\frac{d\theta}{dr},$$

the equation of equilibrium becomes

$$R\frac{\gamma}{\gamma-1}\frac{d\theta}{dr} = -\frac{K}{r^2}\int_0^r 4\pi\rho r^2 dr$$

$$= -\frac{K}{r^2}\int_0^r 4\pi\left(\frac{R\theta}{c}\right)^{\frac{1}{\gamma-1}} r^2 dr. \quad . \quad . \quad (8)$$

Now if the gas loses heat c will diminsh. Let us find the changes in r and θ for the same element of gas—or rather, for the gas occupying the same relative position in the mass, corresponding to a diminution in c. Suppose the new value of c is c_1 such that

$$c_1 = nc,$$

n being less than unity; and let r_1, θ_1 be the new values of r, θ for the corresponding element of gas. Then it can easily be shown that

$$r_1 = n^\alpha r$$

$$\theta_1 = n^\beta \theta$$

satisfy all the conditions of the problem provided α and β be properly chosen. For, the new equation of equilibrium is

$$R\frac{\gamma}{\gamma-1}r_1^2\frac{d\theta_1}{dr_1} = -K\int_0^{r_1} 4\pi\left(\frac{R\theta_1}{nc}\right)^{\frac{1}{\gamma-1}} r_1^2 dr_1. \quad . \quad . \quad (9)$$

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Now putting $n^\alpha r$ for r_1 and $n^\beta \theta$ for θ_1 we find

$$R\frac{\gamma}{\gamma-1}r_1^2\frac{d\theta_1}{dr_1}=R\frac{\gamma}{\gamma-1}r^2\frac{d\theta}{dr}n^{\alpha+\beta} ; \quad . \quad . \quad . \quad (10)$$

and

$$\int_0^{r_1}\left(\frac{\theta_1}{nc}\right)^{\frac{1}{\gamma-1}}r_1^2 dr_1=\int_0^r\left(\frac{n^\beta\theta}{nc}\right)^{\frac{1}{\gamma-1}}r^2 n^{2\alpha}dr$$

$$=n^{\frac{\beta-1}{\gamma-1}+3\alpha}\int_0^r\left(\frac{\theta}{c}\right)^{\frac{1}{\gamma-1}}r^2 dr. \quad . \quad . \quad (11)$$

Hence we see that with these values for r_1, θ_1, equation (9) is reduced to equation (8) provided

$$n^{\alpha+\beta}=n^{\frac{\beta-1}{\gamma-1}+3\alpha} ;$$

i.e., provided

$$\alpha+\beta=\frac{\beta-1}{\gamma-1}+3\alpha. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This means that, if equation (12) holds, $n^\alpha r$ and $n^\beta \theta$ are the distance from the centre and the temperature respectively of an element of gas in convective equilibrium with the value nc for

$\frac{p}{\rho^\gamma}$. Now to ensure that r_1, θ_1 shall refer to the same element

of gas as r, θ referred to in the old state, we must make the mass within the sphere r_1 the same as that which formerly occupied the sphere r. But the expression on the left-hand side of the equation (11) is proportional to this mass in the new state. It will be the same mass as that originally in the sphere r if

$$n^{\frac{\beta-1}{\gamma-1}+3\alpha}=1,$$

or

$$\frac{\beta-1}{\gamma-1}+3\alpha=0. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Equations (12) and (13) give the following values for α and β,

$$\alpha=\frac{1}{3\gamma-4},$$

$$\beta=-\frac{1}{3\gamma-4}.$$

Hence we see that

$$r_1 = n^{\frac{1}{3\gamma-4}} r$$

$$\theta_1 = n^{-\frac{1}{3\gamma-4}} \theta.$$

Now there are two cases to consider.

Case 1. $3\gamma > 4$.

Then, n being less than unity,

$$r_1 < r \; ;$$

that is, the whole sphere contracts uniformly in consequence of loss of heat.

Case 2. $3\gamma < 4$.

Now $r_1 > r \; ;$

that is, the sphere expands uniformly in consequence of loss of heat. In both cases

$$r_1\theta_1 = r\theta.$$

In the first case, therefore, as the gas loses heat the sphere contracts and the temperature rises; whereas, in the second case, with loss of heat the sphere expands and the temperature falls. It is clear that, since a gas for which γ (the ratio of the specific heats) is less than $1\frac{1}{3}$, loses energy as it expands, it must be supplied with energy from outside in order to contract. Also it follows that in any given state of convective equilibrium such a gas has more internal energy than it could have obtained by contraction from a state of infinite diffusion. This conclusion agrees with Perry's theorem as stated by Lord Kelvin, on page 368 of *Nature* for February 14, 1907. If, however, the gas has been supplied by some means with the heat necessary for a state of convective equilibrium, the gradual inevitable loss of heat will only drive the particles further and further apart until the outer portions come within the sphere of attraction of some other body, after which this body will gradually suck in the whole of the gas. But a gas for which γ is greater than $1\frac{1}{3}$ will condense as it loses heat until a liquid nucleus is formed at its centre. After that stage is reached the results obtained for a wholly gaseous mass will no longer apply.

ERRATUM :—" Strength of Brickwork Piers and Concrete.'
In footnote on page 178, for " Medal" read " Premium."

MUNICIPAL SCHOOL OF TECHNOLOGY, MANCHESTER.

The Municipal School of Technology

SACKVILLE STREET, MANCHESTER

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PRINCIPAL - J. H. REYNOLDS, M.Sc.

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A RECORD OF INVESTIGATIONS
UNDERTAKEN BY MEMBERS
OF THE TEACHING STAFF OF
THE SEVERAL DEPARTMENTS
OF THE SCHOOL

MCMIX.

CONTENTS.

THE FIGURE OF THE EARTH.

J. PRESCOTT.

I SHALL assume that the figure of the earth is an oblate spheroid of small ellipticity, and I propose to find this ellipticity. I shall also assume that the figure is the same as it would be if the earth were wholly liquid. There can be little doubt that the figure obtained on these assumptions is not far from the actual shape. For the earth's crust is probably not rigid enough to resist the forces pulling it into this shape. It is necessary first to find the potential, at an external point on the axis, of a thin shell bounded by similar oblate spheroids whose generating curves are

$$\frac{x_1{}^2}{a^2} + \frac{y_1{}^2}{b^2} = 1,$$

$$\frac{x_2{}^2}{a^2} + \frac{y_2{}^2}{b^2} = 1 + \sigma$$

where $\qquad b^2(1+\sigma) = (b+\delta b)^2 = b^2 + 2b\delta b,$

or $\qquad \sigma = 2\dfrac{\delta b}{b};$

and b is the polar semi-axis.

Let P be the external point, O the centre of the shells, $OP = r$, $(a-b) = eb$, $K =$ the gravitation constant, $\rho =$ density. The mass of a thin ring of the shell between the planes y and $y + \delta y$ is

$$\pi\rho(x_2{}^2 - x_1{}^2)\delta y$$

$$= \pi\rho\sigma a^2\delta y.$$

Fig. 1.
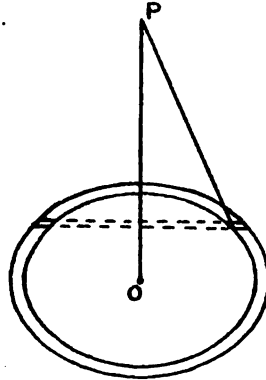
Taking potential to be $\Sigma\dfrac{Km}{r}$, the potential of this ring at P

$$= \frac{K\pi\rho\sigma a^2\delta y}{\sqrt{\{x_1{}^2 + (r-y_1)^2\}}}$$

$$= \mathrm{K}\pi\rho\sigma a^2 \delta y \left\{ a^2\left(1 - \frac{y^2}{b^2}\right) + r^2 - 2yr + y^2 \right\}^{-\frac{1}{2}}$$

$$= \mathrm{K}\pi\rho\sigma a^2 \delta y \left\{ b^2(1 + 2e)\left(1 - \frac{y^2}{b^2}\right) + r^2 - 2yr + y^2 \right\}^{-\frac{1}{2}} \text{ nearly}$$

$$= \mathrm{K}\pi\rho\sigma a^2 \delta y \left\{ r^2 - 2yr + b^2 + 2e(b^2 - y^2) \right\}^{-\frac{1}{2}}$$

$$= \mathrm{K}\pi\rho\sigma a^2 \delta y (r^2 - 2yr + b^2)^{-\frac{1}{2}} \left\{ 1 - e\frac{b^2 - y^2}{r^2 - 2yr + b^2} \right\}$$

where only the first power of e has been retained. The potential of the whole shell

$$= \mathrm{K}\pi\rho\sigma a^2 \int_{-b}^{+b} \left\{ (r^2 - 2yr + b^2)^{-\frac{1}{2}} - e(b^2 - y^2)(r^2 - 2yr + b^2)^{-\frac{3}{2}} \right\} dy$$

$$= \mathrm{K}\pi\rho\sigma a^2 \left[-\frac{1}{r}(r^2 - 2yr + b^2)^{\frac{1}{2}} - e\frac{b^2}{r}(r^2 - 2yr + b^2)^{-\frac{1}{2}} \right]_{-b}^{+b}$$

$$+ e\mathrm{K}\pi\rho\sigma a^2 \int_{-b}^{+b} y^2(r^2 - 2yr + b^2)^{-\frac{3}{2}} dy$$

Now $\int y^2 (r^2 - 2yr + b^2) dy$

$$= \frac{y^2}{r}(r^2 - 2yr + b^2)^{-\frac{1}{2}} + \frac{2y}{r^2}(r^2 - 2yr + b^2)^{\frac{1}{2}} + \frac{2}{3r^2}(r^2 - 2yr + b^2)^{\frac{3}{2}}$$

Hence the potential of the shell

$$= \mathrm{K}\pi\rho\sigma a^2 \left\{ \frac{2b}{r} - e\frac{b^2}{r}\left(\frac{1}{r-b} - \frac{1}{r+b}\right) + e\frac{b^2}{r}\left(\frac{1}{r-b} - \frac{1}{r+b}\right) \right.$$

$$\left. + \frac{2be}{r^2}(r - b + r + b) + \frac{2e}{3r^2}\left\{ (r-b)^3 - (r+b)^3 \right\} \right\}$$

$$= 2\mathrm{K}\pi\rho\sigma a^2 \left\{ \frac{b}{r} - \frac{2eb^3}{3r^3} \right\}$$

$$= 2\mathrm{K}\pi\rho\sigma b^2 [1 + 2e] \left\{ \frac{b}{r} - \frac{2eb^3}{3r^3} \right\}$$

$$= 2\mathrm{K}\pi\rho\sigma b^3 \left\{ \frac{1}{r}(1 + 2e) - \frac{2eb^2}{3r^3} \right\}$$

The potential, at an external point P on its axis, of a homogeneous spheroid whose polar radius is β and eccentricity e, is obtained by putting $2\frac{db}{b}$ for σ in the expression for the potential of a shell and integrating.

Thus the potential

$$= \mathrm{V}_1 = 2\mathrm{K}\pi\rho \int_0^\beta \frac{2db}{b} b^3 \left\{ \frac{1}{r}(1 + 2e) - \frac{2eb^2}{3r^3} \right\}$$

$$= 4 \mathrm{K} \pi \rho \left\{ \frac{\beta^3}{3r} (1 + 2e) - \frac{2}{3} \cdot \frac{e\beta^5}{5r^3} \right\}$$

$$= \frac{4 \mathrm{K} \pi \rho \beta^3}{3} \left\{ \frac{1}{r} (1 + 2e) - \frac{2e\beta^2}{5 r^3} \right\}$$

Since the potential of the spheroid at an external point is a zonal harmonic, we find that the potential at any external point is

$$\mathrm{V}_2 = \frac{4 \mathrm{K} \pi \rho \beta^3}{3} \left\{ \frac{1}{r} (1 + 2e) - \frac{2e\beta^2}{5 r^3} \left(\frac{3 \cos^2 \theta - 1}{2} \right) \right\}$$

where r is the length of the radius vector from the centre of the spheroid to the point, and θ is the angle between this radius vector and the axis of symmetry. Now suppose the earth is so composed that layers of equal density are the surfaces of spheroids of varying ellipticity, the surface of the earth itself being one of these spheroids. We may consider the density of any layer and its ellipticity to be functions of the polar semi-axis of the layer. Let $\delta \mathrm{V}$ be the potential at r, θ of one of these layers. Then

$$\mathrm{V} = \frac{4}{3} \mathrm{K} \pi \rho \frac{d}{d\beta} \left\{ \frac{1}{r} (1 + 2e) \beta^3 - \frac{1}{5r^3} e\beta^5 (3 \cos^2 \theta - 1) \right\} \delta \beta .$$

The potential of the earth, regarded as a heterogeneous spheroid such as I have supposed, its polar radius being R, is

$$\mathrm{V}_3 = \frac{4}{3} \mathrm{K} \pi \int_0^{\mathrm{R}} \rho \frac{d}{d\beta} \left\{ \frac{1}{r} (1 + 2e) \beta^3 - \frac{1}{5r^3} e\beta^5 (3 \cos^2 \theta - 1) \right\} d\beta$$

$$= \frac{4}{3} \mathrm{K} \pi \left\{ \frac{\mathrm{A}}{r} - (3 \cos^2 \theta - 1) \frac{\mathrm{B}}{5r^3} \right\}$$

where

$$\mathrm{A} = \int_0^{\mathrm{R}} \rho \frac{d}{d\beta} (1 + 2e) \beta^3 d\beta$$

and

$$\mathrm{B} = \int_0^{\mathrm{R}} \rho \frac{d}{d\beta} (e\beta^5) d\beta .$$

By putting $r = \mathrm{R}$ and $\theta = 0$ in the expression for V_3 we find that the potential at the end of the polar radius

$$= \frac{4}{3} \mathrm{K} \pi \left\{ \frac{\mathrm{A}}{\mathrm{R}} - \frac{2\mathrm{B}}{5\mathrm{R}^3} \right\}$$

And by putting $r = \mathrm{R}(1 + \epsilon)$ [ϵ being the value of e at the earth's surface] and $\theta = \frac{\pi}{2}$, the value of the potential at the earth's surface on the equator is found to be

$$\frac{4}{3} \mathrm{K} \pi \left\{ \frac{\mathrm{A}}{\mathrm{R}(1 + \epsilon)} + \frac{\mathrm{B}}{5\mathrm{R}^3 (1 + \epsilon)^3} \right\}$$

$$= \frac{4}{3} K\pi \left\{ \frac{A}{R} - \epsilon \frac{A}{R} + \frac{B}{5R^3} \right\}$$

Since B already contains the first power of e we do not need to retain ϵB &c. The potential of centrifugal force at the equator, due to the earth's rotation, is

$$\tfrac{1}{2}R^2(1+\epsilon)^2\omega^2 \text{ or } \tfrac{1}{2}R^2\omega^2,$$

(ω being the earth's angular velocity of rotation) provided we assume, as in the case of attractions, that the space variation of potential gives the force on unit mass, and not the negative of this force as is usual. Since the earth's surface is a level surface the whole potential at the equator is equal to the whole potential at the pole. Hence

$$\frac{4}{3} K\pi \left\{ \epsilon \frac{A}{R} - \frac{3B}{5R^3} \right\} = \frac{1}{2} R\omega^2.$$

Now

$$\frac{4}{3} \pi A = \int_0^R \rho \frac{d}{d\beta} \left(\frac{4}{3}\pi\beta^3 \right) d\beta$$

$$= E, \text{ the earth's mass.}$$

Also

$$\frac{KE}{R^2} = g, \text{ the acceleration due to gravity at the earth's surface.}$$

Thus we get

$$\epsilon R g - \frac{4}{3} K\pi \frac{3B}{5R^2} = \frac{1}{2} R^2 \omega^2,$$

or

$$\epsilon \frac{g}{R\omega^2} - \frac{4}{3} K\pi \frac{3}{5} \cdot \frac{B}{R^5\omega^2} = \frac{1}{2}. \quad \ldots \ldots \quad (\alpha)$$

If ρ is constant then e may be considered constant and $B = \rho\epsilon R^5$. Then our equation would give

$$\epsilon \frac{g}{R\omega^2} - \frac{3}{5} \epsilon \frac{g}{R\omega^2} = \frac{1}{2}.$$

But

$$\frac{g}{R\omega^2} = 289.$$

Hence

$$\frac{1}{\epsilon} = 231.$$

It is certain, however, that e is not constant. We cannot find ϵ therefore without knowing the value of the coefficient B. Now this coefficient is given in terms of $\int_0^R \rho\beta^4 d\beta$, a quantity which does not contain e, by the theory of the precession of the earth's axis. By assuming a reasonable law for ρ we can then find B, and thence determine ϵ.

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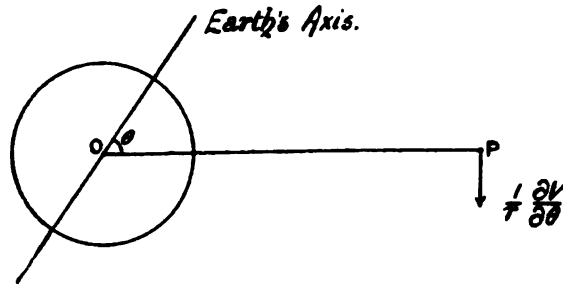
Fig. 2.

The potential of the earth at an external point P (fig. 2) is

$$V = \frac{4}{3} K\pi \left\{ \frac{A}{r} - \frac{B}{5r^3} (3 \cos^2 \theta - 1) \right\}$$

The force exerted by the earth perpendicular to OP on unit mass at P is

$$\frac{\delta V}{r \delta \theta}$$

The moment of this force about O is $\frac{\delta V}{\delta \theta}$. Now the reaction of the unit mass on the earth is exactly the opposite of the earth's action on the unit mass. Consequently the moment about O of the couple exerted by the unit mass on the earth is $\frac{\delta V}{\delta \theta}$ in the direction tending to increase the angle θ up to a right angle. If the sun is at P, the couple exerted by the sun, whose mass is S, is

$$S\frac{\delta V}{\delta \theta} = S\frac{8}{5}K\pi \frac{B}{r^3} \cos \theta \sin \theta.$$

If n is the angular velocity of the earth in its orbit

$$\frac{KS}{r^3} = rn^2.$$

Thus the couple exerted by the sun on the earth becomes

$$\tfrac{8}{5} \pi Bn^2 \sin \theta \cos \theta.$$

Referring to figure 3, by spherical trigonometry, $\cos \theta = \sin \alpha \sin \phi$.

Therefore $\sin \theta = \sqrt{\{ 1 - \sin^2 \alpha \sin^2 \phi \}}$

$$= 1 - \tfrac{1}{2} \sin^2 \alpha \sin^2 \phi + \tfrac{3}{4} \sin^4 \alpha \sin^4 \phi$$

nearly, since $\sin \alpha = \sin 23\tfrac{1}{2}° = \cdot 4$ about, so that the terms ignored are small.   Hence the couple exerted by the sun

$$= \tfrac{8}{5} \pi Bn^2 \sin \alpha \sin \phi \{ 1 - \tfrac{1}{2} \sin^2 \alpha \sin^2 \phi + \tfrac{3}{4} \sin^4 \alpha \sin^4 \phi \}.$$

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Fig. 3.
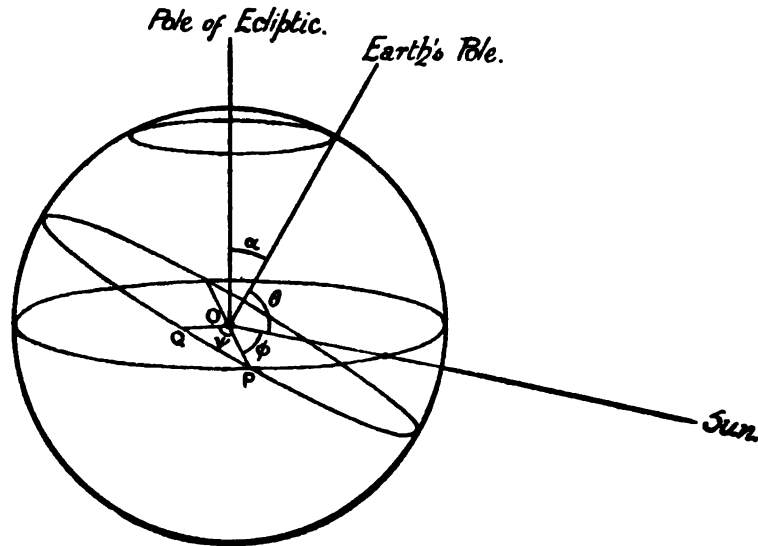
The axis of this couple is O Q, perpendicular to the plane containing the earth's axis and the sun. The only effective component in precession is that parallel to O P, the intersection of the plane of the equator and the ecliptic. The other component causes nutation. Hence the effective couple for precession

$$= \text{moment of couple} \times \cos \Psi.$$

By spherical trigonometry

$$\cos \Psi = \frac{\sin \phi}{\sqrt{(1 + \tan^2 a \cos^2 \phi)}}$$

$$= \sin \phi (1 - \tfrac{1}{2} \tan^2 a \cos^2 \phi + \tfrac{3}{8} \tan^4 a \cos^4 \phi).$$

Thus the effective couple is

$$L = \frac{8\pi}{5} Bn^2 \sin a \sin^2 \phi \{ 1 - \tfrac{1}{2} \sin^2 a \sin^2 \phi - \tfrac{1}{2} \tan^2 a \cos^2 \phi$$

$$+ \tfrac{3}{8} \sin^4 a \sin^4 \phi + \tfrac{1}{4} \tan^2 a \sin^2 a \sin^2 \phi \cos^2 \phi$$

$$+ \tfrac{3}{8} \tan^4 a \cos^4 \phi \}.$$

Now $\frac{d\phi}{dt} = n$. Therefore $dt = \frac{d\phi}{n}$. Hence the moment of momentum generated by the sun's couple action in one year

$$= \int_0^{2\pi} L \frac{d\phi}{n}$$

$$= \frac{8}{5} Bn\pi \sin a \cdot \pi \left\{ 1 - \frac{1}{2} \sin^2 a \cdot \frac{3}{4} \cdot \frac{1}{2} \cdot 2 - \frac{1}{2} \tan^2 a \cdot \frac{1}{4} \cdot \frac{1}{2} \cdot 2 \right.$$

$$+ \frac{3}{8} \sin^4 a \, \frac{5}{6} . \frac{3}{4} . \frac{1}{2} . 2 + \frac{1}{4} \tan^2 a \sin^2 a \, \frac{1}{2} . \frac{3}{4} . \frac{1}{2} . 2$$

$$+ \frac{3}{8} \tan^4 a . \frac{1}{2} . \frac{3}{4} . \frac{1}{2} . 2 \Big\},$$

which becomes, on putting $23\frac{1}{2}°$ for a,

$$\tfrac{8}{5} \, B n \pi^2 \sin a \{ \cdot 931 \}.$$

This is the sun's effect. The moon's effect must be added to this. The mean place of the moon is in the ecliptic, and if the action of the moon be taken to be the same as that of a similar body always in the ecliptic at the moon's distance the error will be small.

Let S, E, M denote the sun's, earth's, and moon's masses; d_s, d_M the sun's and moon's distances from the earth : then

$$\frac{\text{Moon's effect}}{\text{Sun's effect}} = \frac{\dfrac{M}{d^3_M}}{\dfrac{S}{d^3_s}}$$

$$= \frac{M}{M + E} \frac{\dfrac{E + M}{d^3_M}}{\dfrac{S}{d^3_s}}$$

$$= \frac{1}{82} \frac{\dfrac{1}{(\text{Moon's Period})^2}}{\dfrac{1}{(\text{Earth's Period})^2}}$$

$$= \frac{1}{82} \left(\frac{365\frac{1}{4}}{27 \cdot 3} \right)^2$$

$$= 2 \cdot 18 \text{ about.}$$

Hence the effective moment of momentum created by the combined action of the sun and moon

$$= 3 \cdot 18 \times \tfrac{8}{5} \, \pi^2 B n \sin a (\cdot 931).$$

If I is the moment of inertia of the earth and ω, as before, its angular velocity of rotation, this effect turns the earth's axis through

$$\frac{3 \cdot 18 \times \tfrac{8}{5} \, \pi^2 n B \sin a (\cdot 931)}{I \omega} \text{ radians.}$$

But the earth's axis describes a cone of semi-vertical angle a in 26,000 years. Hence the angle turned through by the earth's axis in one year is

$$\frac{2\pi \sin a}{26000}$$

Therefore $\qquad \dfrac{\cdot 931 \times 3 \cdot 18 \times \frac{8}{5} \ \pi^2 \text{B}n \sin a}{\text{I}\omega} = \dfrac{2\pi \sin a}{26000}$

Whence $\quad \text{B} = \dfrac{2 \times 5}{26000 \times \cdot 931 \times 3 \cdot 18 \times 8\pi} \cdot \dfrac{\omega}{n} \text{I}$

$\qquad = \dfrac{10}{26000 \times \cdot 931 \times 3 \cdot 18 \times 8\pi} \ \dfrac{365\frac{1}{4}}{1} \ \dfrac{2}{3} \int_0^R 4\pi\rho\beta^4 d\beta$

$\qquad = \dfrac{5}{316} \int_0^R \rho\beta^4 d\beta.$

If ρ were constant, in which case we could consider e constant also, this would give

$$\epsilon = \dfrac{1}{316},$$

which does not agree with the result found by assuming ρ to be constant in the equation obtained by considering the equilibrium shape of a liquid earth.

We shall now have to assume an expression for ρ in terms of the radius which shall agree with all known facts, and give a density decreasing from the centre outwards. We know that, the density of water being taken as the unit, the mean density of the earth is about 5·5 and the surface density is 3 or 2·5.

Also it is quite certain that ρ decreases from the centre outwards. These facts tell us that

$$\int_0^R \rho\beta^4 d\beta > 2 \cdot 5 \times \tfrac{1}{5} \ \text{R}^5$$

and $\qquad\qquad\qquad\qquad\qquad < 5 \cdot 5 \times \tfrac{1}{5} \ \text{R}^5.$

The first of these conclusions is easily seen; for at every point in the earth

$$\rho\beta^4 > 2 \cdot 5\beta^4 \ ;$$

and therefore $\qquad \displaystyle\int_0^R \rho\beta^4 d\beta > 2 \cdot 5 \times \tfrac{1}{5} \ \text{R}^5.$

The second statement can be proved thus :—

We know that $\qquad \displaystyle\int_0^R \rho\beta^2 d\beta = 5 \cdot 5 \times \tfrac{1}{3} \ \text{R}^3.$

Therefore $\qquad \dfrac{3\text{R}^2}{5} \displaystyle\int_0^R \rho\beta^2 d\beta = \dfrac{5 \cdot 5}{5} \ \text{R}^5.$

Hence $\dfrac{5 \cdot 5}{5} \text{R}^5 - \displaystyle\int_0^R \rho\beta^4 d\beta = \dfrac{3\text{R}^2}{5} \displaystyle\int_0^R \rho\beta^2 d\beta - \displaystyle\int_0^R \rho\beta^4 d\beta$

$\qquad\qquad = \dfrac{1}{5}\left[\rho\text{R}^2\beta^3 - \rho\beta^5 \right]_0^R - \displaystyle\int_0^R \dfrac{1}{5}(\text{R}^2\beta^3 - \beta^5)\dfrac{d\rho}{d\beta} \ d\beta$

$$= -\frac{1}{5} \int_0^R \beta^2 (R^3 - \beta^3) \frac{d\rho}{d\beta} d\beta.$$

Now $\frac{d\rho}{d\beta}$ is always negative and the remaining factors under the integral sign are positive. Thus

$$\frac{5 \cdot 5}{5} R^5 = \int_0^R \rho \beta^4 d\beta + \text{a positive quantity,}$$

which proves the second statement.

A law of density which gives roughly the type of variation to be expected is

$$\rho = C - D \left(\frac{\beta}{R}\right)^n$$

To make $\rho = 3$ at the surface we get

$$3 = C - D.$$

C is the density at the centre and can be given any arbitrary value. By making the mean density $5 \cdot 5$, n is determined thus :—

$$\int_0^R \rho \beta^2 d\beta = 5 \cdot 5 \int_0^R \beta^2 d\beta.$$

This gives

$$C - \frac{3}{n+3} D = 5 \cdot 5.$$

But also

$$C - D = 3.$$

Therefore

$$n = \frac{15}{2C - 11}.$$

Let m denote the value of

$$\frac{\int_0^R \rho \beta^4 d\beta}{\int_0^R \beta^4 d\beta}.$$

Then

$$m = C - \frac{5}{n+5} D$$

$$= 4 \cdot 5 + \frac{3}{2C - 8}$$

on substituting for n and D.

Now the densest materials we know in the earth's crust have specific gravities only about 22 or 23. It is highly probable then that the density at the earth's centre is not more than 30. The fact that we find in the earth's crust matter so dense as platinum and osmium mingled with much lighter substances, rather indicates that the density at the centre is not nearly so great as 30. For, if substances of such different densities are to be found within a few feet of the earth's surface, it is very likely that lighter matter will

be mingled with the denser in the interior. But at the same time there must be a gradual increase of density from the surface towards the centre.

When we have determined m the value of B can be calculated from the equation

$$B = \frac{5}{316} m \frac{1}{5} R^5$$

$$= \frac{m}{316} R^5$$

Substituting for B in equation (a), obtained from the rotation of the earth, we find

$$\epsilon \frac{g}{R\omega^2} = \frac{4}{5} K\pi \frac{m}{316} \frac{R^5}{R^5\omega^2} + \frac{1}{2}$$

$$= \frac{3}{5} \frac{1}{316} \cdot \frac{m}{5.5} \frac{KE}{R^2} \cdot \frac{1}{R\omega^2} + \frac{1}{2}$$

$$= \frac{3}{5} \frac{1}{316} \cdot \frac{m}{5.5} \cdot \frac{g}{R\omega^2} + \frac{1}{2}$$

Now
$$\frac{g}{R\omega^2} = 289$$

Hence
$$\epsilon = \frac{3m}{5 \times 316 \times 5.5} + \frac{1}{2} \frac{1}{289}$$

The following table gives the calculated values of ϵ, using the value of m obtained by assuming

$$\rho = A - B \left(\frac{\beta}{R}\right)^n$$

Density at the surface.	Density at the centre.	Mean Density.	$\frac{1}{\epsilon}$
3	30	5·5	303
3	25	5·5	303
3	20	5·5	302
3	15	5·5	300
3	13	5·5	300
3	12	5·5	299
3	10	5·5	297
2·5	30	5·5	310
2·5	25	5·5	309
2·5	20	5·5	307
2·5	15	5·5	306
2·5	10	5·5	299

It appears from the above table that the value assumed for the density at the centre does not greatly affect the result. I believe tnat any assumption concerning the density, which makes it decrease as the radius increases and which gives approximately the known

mean and surface densities, cannot give a value of ϵ differing much from those in the table. I tried another completely different formula for the density to see what result it led to. The formula is

$$\rho = \frac{H}{(\beta + K)^3}.$$

To make the surface density 3 and the mean density 5·5, I found that H and K must be 16·35R³ and ·76R respectively. These values make the density at the centre very large, namely, 37·2. The value found for m is 4·68. This gives

$$\frac{1}{\epsilon} = 299$$

The value I consider most probable from my calculations is

$$\frac{1}{\epsilon} = 303$$

EXPLANATORY NOTE.

The "Journal of the School of Technology" was established for the purpose of recording the original scientific work done in the School by members of the teaching staff or by students. But in view of the large accumulation of such work during the last seven or eight years, considerable time would have elapsed before the records could be brought up to a recent date. In the meantime the value of the later publications might have considerably decreased, and it was therefore thought advisable to print in abstract only, or, in some cases, the titles only, of all the work published previous to the year 1908 which has not been already printed in the "Journal." The papers for 1908 will be published in full, and it is expected that the work of the following years will appear in the "Journal" within a short time of their original publication.

AN INVESTIGATION TO DETERMINE THE EFFECTS OF STEAM JACKETING UPON THE EFFICIENCY OF A HORI-ZONTAL COMPOUND STEAM ENGINE. A. L. MELLANBY. "Proceedings of the Institution of Mechanical Engineers," June, 1905. Tests were carried out by the author with the large experimental engine of the School of Technology, which is described on pages 11 to 20 of this "Journal." In each trial the boiler pressure was 150 lbs, and the speed approximately 59 revolutions per minute. The trials were made with four different ratios of expansion—the first set with 8·1 total expansions; second with 12·3; third with 18, and the fourth with 25. For each corresponding point of cut-off in the high-pressure cylinder five tests were made, except for the last, for which three tests only were made : (1) with both cylinders unjacketed; (2) with the ends of the high-pressure cylinder jacketed; (3) with the ends and barrel of the high-pressure cylinder jacketed; (4) with the ends and barrel of the high-pressure cylinder and ends of the low-pressure cylinder jacketed; (5) with the ends and barrels of both cylinders jacketed. The driving gear was disconnected from the governor, and by means of an arrangement which allowed the governor sleeve to be raised or lowered, the point of cut-off in the high-pressure cylinder could be fixed at any point of the stroke. The results are given in tables showing the weight of steam used in the various jackets or passed through the cylinders, steam used per I.H.P. per hour, etc. For each condition of jacketing a diagram is given showing the variation with the ratios of expansion of the following :—Steam per I.H.P. per hour; total steam per hour; indicated weight of steam at release; indicated weight at cut-off; I.H.P.; missing quantity at cut-off; missing quantity at release. By comparing the amount of steam in the cylinders at different points of the stroke, as shown by the indicator diagrams, with that found by calculation on the assumption that the missing quantity is due to condensation at admission, the author finds confirmation of the conclusion of Messers. Callender and Nicolson, that the missing quantity is largely due to valve leakage. The results of the trials are summarised as follows :—

(1) Best mean pressure. That compound condensing engines with a boiler pressure of 150 lbs. may be worked with a mean pressure referred to the low-pressure cylinder of about 40 lbs. per square inch without any loss of efficiency in terms of the brake horse-power.

(2) Maximum efficiency. That the jackets have their maximum efficiency when the whole of the high-pressure cylinders and the ends of the low-pressure cylinders are jacketed with high-pressure steam.

(3) Variation of indicated horse-power. That when the jackets are applied to the high-pressure cylinder the total indicated horse-power is slightly reduced, but when applied to the low-pressure cylinder the total indicated horse-power is considerably increased.

(4) Initial condensation. That the jackets have little effect in

the high-pressure cylinder, but have a considerable effect in the low-pressure cylinder upon initial condensation.

(5) Temperature cycle of metal. That the temperature cycle of the cylinder walls next to the steam must be considerably less than that of the steam, *(a)* because the actual missing quantity is much less than it would have been had the steam and metal gone through the same temperature changes, *(b)* because the mean temperature of the metal is higher than that of the steam.

(6) Missing quantity. That the greater part of the missing quantity must be due to leakage and not to initial condensation *(a)* because the application of the methods suggested by Messrs. Callender and Nicolson shows the condensation to be but a small fraction of the missing quantity, *(b)* because the apparent re-evaporation during expansion is less for jacketed than for unjacketed engines.

The paper is illustrated by eighteen figures in the letterpress, and is accompanied by an appendix.

EXPERIMENTS WITH A LATHE-TOOL DYNAMOMETER. J. T. NICOLSON. "Proceedings of the Institute of Mechanical Engineers," Chicago, June, 1904, and the "Proceedings of the American Society of Mechanical Engineers," Chicago, June, 1904. This paper describes the construction and operation of a force-measuring instrument for use with a turning tool in a lathe. The apparatus is constructed to measure the forces operative in all three co-ordinate directions when a tool is taking off a shaving of metal. A large number of experiments with this apparatus are reported upon, which were made upon billets left over from the Manchester Committee's experiments on the durability of rapid-cutting steels. The paper is in some sense complementary to that Committee's report. The durability experiments give information as to the most economical speeds at which the high-speed steels should be run; having regard to both waste of steel and waste of time. The force-measuring experiments tell what strains may be expected in the various elements of the machine tool when cuts of different areas are being taken at their most economical speeds.

Both of these lines of data are fundamental to the rational design and use of metal-cutting machines.

MACHINE-TOOL DESIGN AS AFFECTED BY THE USE OF HIGH-SPEED CUTTING TOOLS. J. T. NICOLSON. "Transactions of the Institution of Civil Engineers," Engineering Conference, 1907. The design of the lathe, the most important of all machine-tools, has been greatly modified by the introduction of the high-heat steels. Much greater power, strength and rigidity are now necessary, and many faults of construction, always existing, have been laid bare by the severe tests imposed by the use of the new steel.

Power. The power required depends upon the area of the cut, the force upon the tool, and the speed with which the cut is taken. The first factor depends upon the size and nature of the work. In repetition work, forging can be done closely to size, and only fine cuts need be taken. This appears to be the reason why American lathes are, on the whole, lighter than those of British design. · In general engineering work, however, lathes which can take heavy roughing cuts are necessary, for it is cheaper to forge only approximately to size, and afterwards remove the excess material in the lathe, when a small number of pieces of any one kind are required. The amount which may nowadays be economically left on a forging is greater than it was, because it is less costly to produce a ton of shavings with high-heat steel than with low heat; not because the work required to machine off the ton is any less, but because the on-cost charge is smaller. This remark suggests that the "standard cut," by which is meant the size of the shaving which the lathe is designed to remove (on machinery steel), might reasonably be fixed at a higher value now than formerly. In the comparisons which follow this has not been done, however, but a cut having a depth equal to one-fortieth of the height of centres and a traverse feed one-quarter of this have been assumed : a result based on data collected from practice.

With regard to the second factor number two, it is now known that the vertical pressure exerted on the point of a tool of ordinary shape is 100 tons per square inch for soft steel, and about 80 tons per square inch for cast iron. These figures appear not to vary much with either the area of the cut or its shape, and to be, to a first approximation, independent of the speed. The cutting force is thus the same whether carbon or high-heat steel is being used, and, the standard cut having been assumed the same for both, the power required will depend only on the speed of cutting.

This leads us to the third factor, the cutting speed. As will appear from an inspection of the accompanying table, the high-heat steel has increased the speed about threefold for the heavy and moderate cuts, and about five- to seven-fold for light cuts. The power required is therefore from three- to seven-fold as great for high- as for low-heat steel :—

CUTTING SPEEDS FOR HIGH- AND LOW-HEAT STEELS COMPARED.

Depth of Cut.	Traverse Feed.	Area of Cut.	Speed with Carbon Steel.	Speed with High-heat Steel.
Inch.	Inch.	Square Inch.	Feet per minute.	Feet per minute.
$\frac{1}{4}$	$\frac{1}{60}$	0·005	20	150
$\frac{1}{4}$	$\frac{1}{16}$	0·01	20	110
$\frac{1}{2}$	$\frac{1}{10}$	0·05	16	50
1	$\frac{1}{10}$	0·10	13	40
1	$\frac{1}{5}$	0·20	10	30

POWER REQUIRED FOR LATHES WITH HIGH- AND LOW-HEAT STEELS COMPARED.

Height of Centres.	6 inches.	12 inches.	18 inches.	36 inches.	60 inches.
	H.P.	H.P.	H.P.	H.P.	H.P.
Power for carbon steel.......	1	3¼	6¼	16	25
Power for high-heat steel....	7	13	19	50	75

Heavy cuts are more economical than light, if both are taken at their appropriate speeds, because :—(1) The high-heat steel will cut a greater weight per unit of time, without damage; (2) the gross power is less per unit of weight machined.

Highest and Lowest Spindle-speeds, and their Ratio. These data are fundamental to the design of the fast headstock; and the following figures, rationally deduced, have been confirmed by practice :—

Height of Centres.		6 inches.	12 inches.	18 inches.	36 inches.	60 inches.	
Spindle speeds for carbon-steel lathes...	Greatest.. Least	300 ⎱ 50 6 ⎰	150 ⎱ 50 3 ⎰	102 ⎱ 60 1·7 ⎰	50 ⎱ 100 0·5 ⎰	30 ⎱ 180 0·16 ⎰	Ratio
Spindle speeds for high-heat steel lathes...	Greatest.. Least	600 ⎱ 10 60 ⎰	300 ⎱ 30 10 ⎰	200 ⎱ 50 4 ⎰	100 ⎱ 100 1 ⎰	60 ⎱ 120 0·5 ⎰	Ratio

From this table it is seen that the highest spindle-speed has been doubled throughout, whilst the lowest spindle-speed has been increased tenfold for the smaller, and about twofold for the larger sizes. Thus the ratio of the greatest to the least is not so great as it was for the carbon-steel lathes. This means that, as the number of different spindle-speeds to be provided depends on that ratio, so many speeds and gears are not required for high-speed lathes as were necessary to secure a proper subdivision in a case of carbon-steel lathes; this being more especially true for the smaller sizes.

The Belt-drive. To enable them to transmit the great powers now required much higher belt-speeds have become necessary. In the old lathes, which always had their cones mounted on the spindle, the belt-speed was limited, by the necessity of connecting that cone to the spindle for direct driving, to between 600 and 1,200 feet per minute. This bad practice has now been abandoned by most of the good makers, the cone being placed on a back-shaft and geared down to the spindle by spur and pinion. In this way speeds through the air of 2,000 or 3,000 feet per minute can easily be obtained, and unduly wide belts avoided. The efficiency of the belt-drive is also improved by using large pulleys running at moderate speeds, rather than small pulleys running at very high rates of revolution.

In obtaining the required number of different spindle-speeds it has been found to be better, from the point of view of a good belt-drive, to secure them by increasing the number of back-gears rather than

by adding to the number of the cone-steps or of the counter-shaft speeds. The former method is naturally accompanied by a larger first cost; but the ultimate economy is entirely in the purchaser's favour.

Gears. Tooth-durability has now to receive more attention than formerly. All wheels must be machine-cut, and the proportion of width to pitch very much increased. These broad wheels with finely pitched teeth are conducive to smooth running. Small arcs of approach and enlarged arcs of recess should also be used to secure durability or reduce wear.

Spindles and their Bearings. There seems at first to have been a tendency to increase unduly the diameters of the front bearings of spindles for high-speed lathes. The torques, are, however, no greater than before, and as the power is—at all events, for all but the smaller sizes—transmitted through the face-plate and not through the spindle, the reason for the large increases of diameter to be found in practice is not very obvious. Increased rigidity is, no doubt, required to withstand the shocks, which are greater at higher speeds; but, in the author's opinion, the lack of rigidity has been frequently due to elaborate and defective arrangements for adjustment in the main bearings. The adoption of solid bush-bearings, without any means of adjustment whatever, but fitted with forced lubrication to prevent metal-to-metal contact at the lower speeds, and so altogether to avoid wear, appears to offer a solution of the problem which will enable spindles of smaller diameters and bearings of about half their present length to be used.

Beds and Saddles. The greater vibration set up at high speeds of cutting by reason of the greater liability to resonance, necessitates stiffer beds than before. The time-honoured double H section of bed will ultimately have to be abandoned, and a bed of box or circular section substituted for it. The discrepancy between the strengths of the old-fashioned and the proposed sections, whether for resisting, bending, or torsion, is so great as to render the retention of the old design simply a ludicrous adherence to preconceived notions. Saddles have probably always been rather wabbly; but the high-heat steel has effectually laid bare their weaknesses.

Loose Headstocks. For high-speed turning, the loose headstock needs to be very firmly bolted down at its four corners, and not at the middle. From this point of view it is bad practice to do taper turning by setting over the head. The increased number of joints and the position of the work between centres are against heavy cutting with success.

Feeding Mechanism. All the feed-motions should now be fitted with interlocking devices, and the feed should have a safety throw-out. The high speeds now used do not give the operator any chance of remedying mistakes. Any increase of the number of feed-changes

above four, or at most six, is superfluous, and is a positive disadvantage, if the screw-cutting feed is taken through these gears.

FRICTION AND LUBRICATION. J. T. NICOLSON. "Proceedings of the Manchester Association of Engineers," November 23, 1907. The object of this paper is to obtain a formula for the design of bearings running under a steady non-reversed load, under conditions of "perfect-film" lubrication. The experiments of Stribeck and Heimann are first used to obtain the laws of the variation of the frictional resistance of a lubricant, as dependent upon pressure, temperature and speed; and it is shown that this resistance, for a given temperature, passes through a minimum value as the speed diminishes to nothing, the speed at which this occurs depending on the bearing pressure. This minimum is the result of the joint influence of two factors. One is the diminution of resistance due to the falling speed; the other is the increased resistance produced by the greater eccentricity of the journal as the speed gets less. At a certain speed, which depends on the pressure, the oil film becomes so thin at one part of the journal surface that rupture of the film is very liable to occur; with the result that journal and bearing enter into metallic contact, and the friction increases very quickly up to Morin's value for greasy metals. The speeds at which film-rupture and the minimum value of the resistance occur are, if not coincident, very nearly the same. If, then, it is desired to have a bearing which carries its load at a given speed with an unbroken film, the proportions must be so chosen that the final temperature will not reach a value where the frictional resistance approaches a minimum under the pressure due to the load.

THE USE OF THE TERM "ELASTIC LIMIT" IN METALS UNDER STRESS. W. C. POPPLEWELL. "Engineering Review," April, 1904. The principal object of this paper is an endeavour to make clear the meaning of the term which appears in the title. It begins by enumerating and describing the true meaning of the various phenomena to which the above term has been and is frequently applied. Attention is drawn to the fact that there are three fairly well defined limits found during the loading of iron and steel, namely, the true elastic limit, the limit of proportionality and the yield point. Of these the first two are shown from experimental results to be practically coincident, an opinion which is confirmed by Fremont. Calling these two by the same name, the P limit, it is pointed out that this is relatively the more difficult to determine accurately, and involves the use of instruments of high precision. In most commercial tests it is only the "yield point" that is required, a point easy to determine, but which is often erroneously called the "elastic limit." Besides the objections to this use of the term mentioned earlier in the paper, it is pointed out that many of the high carbon steels show no yield point, and a limit can only be found by the employment of instruments of precision.

ACCURACY IN TESTING MATERIALS. W. C. POPPLEWELL. "Engineering Review," August, 1904. The early part of this paper is devoted to a general discussion of the different stages in the design of a typical structural part, such as a tension bar in a lattice girder bridge, and the part which a knowledge of the strength properties of the material takes. This is followed by an investigation of the accuracy with which stresses in test bars are determined, dealing especially with the accuracy and precision of testing machines and the accuracy with which it is possible to measure the area of the specimen and the elongations and reduction in area. In dealing with the accuracy of testing machines, the writer describes some experiments carried out during the calibration of one of the testing machines in the Testing Laboratory of the Manchester School of Technology. The results of these experiments went to show that in this particular machine the readings of the scale when compared with dead weights showed a mean error of about 2% at a load of 2½ tons, this error diminishing as the loads increased, until at 10 tons, when it was still more slowly decreasing, the mean error was about three-quarters of one per cent.

EXPERIMENTS ON THE RELATION BETWEEN UNIFORM COMPRESSIVE STRESS AND PERMANENT STRAIN IN WROUGHT IRON AND STEEL. W. C. POPPLEWELL. "Memoirs of the Manchester Literary and Philosophical Society," February, 1905. The experiments described in this paper were made for the purpose of establishing a relation between the compressive stress and the permanent strain produced in short cylinders of wrought iron and steel. This relation is expressed by an equation of the form $p = C \cdot e^k$ where p is the stress on the bar, e the ratio of the elongation to the original length, and C and k constants varying with the material tested. The results of the experiments are shown below :—

Material.	Number.	k Side.	k End.	C Side.	C End.
High grade wrought iron........	1...	...	0·251	...	57·56
" "	2...	...	0·265	...	55·33
" "	3...	...	0·267	...	53·61
" " Mean...		...	0·261	...	55·30
Low grade wrought iron.........	4...	0·178	0·172	49·68	50·82
Average mild steel, annealed...	5...	0·234	0·230	61·98	63·43
" " "	6...	0·268	0·264	64·87	68·77
" " "	7...	0·238	0·233	60·64	63·70
" " "	8...	0·264	0·255	64·96	65·35
" " " Mean...		0·251	0·245	63·11	65·31

The experiments described were carried out in the Engineering Laboratory of the Yorkshire College, Leeds, and in the Materials Testing Laboratory of the Manchester School of Technology.

SHEAR STRESS AND PERMANENT ANGULAR STRAIN.

W. C. POPPLEWELL. "The Engineer," January 19, 1906. Recent experiments upon the cutting action of turning tools, when operating upon steel, have yielded results in which the relation between the shearing stress in the material and the angular distortion which it causes is found to play an important part. The results which are given here were arrived at from the results of experiments published in 1895 in the "Proceedings of the Institute of Civil Engineers," vol. cxxii. In this paper is described a series of experiments upon the torsional strength of solid and hollow shafts. Working from these same results, the writer has deduced the further figures which are given here.

Consider a short length of a circular shaft, of which l is its length, A B is a line drawn upon its surface before any distortion has taken place, and O A is a radius of the shaft drawn from a centre O to a point on the surface A, also previous to the application of a torque. On the shaft being subjected to a torsional moment, the two bounding circular sections will be rotated relatively to one another, and the radius O A will be moved into a new position O C, and at the same time the line B A will be correspondingly deflected into a new position B C. The angle A B C is called here the "angle of distortion" of the material on the surface, and

$$\tan \alpha = \frac{A C}{A B}.$$

The problem was to find a relation between the shear stress at the surface of the shaft and the angle of distortion α. The method followed was this :—

From the readings taken, during the experiments, of the twisting moments and their corresponding angles of twist, the several angles α were found. The kind of figures obtained are shown in Table I.

In order to find out the relation existing between T and α, the writer plotted the logarithms of the twisting moments against those of the angles of distortion. The logarithmic graph for each experiment consists, not of one straight line, as might have been expected, but of two consecutive straight lines, the second having a less inclination than the first. The logarithmic plottings yield two equations for each shaft, one belonging to the lower portion of the graph and the second to the latter part. They are :—

$$T = A . \alpha^m, \text{ for the lower part,}$$
and
$$T = B . \alpha^n, \text{ for the upper part.}$$

In these equations the four constants A, B, m and n depend upon

TABLE I.—FIVE HOLLOW MILD STEEL SHAFTS.

T Twisting moment, inch-pounds.	Angles of distortion (a), in degrees.				
	16	17	18	19	20
500	0·75	1·90	1·25	1·90	1·30
550	2·50	2·65	2·30	2·70	2·26
600	3·20	3·65	3·10	3·50	3·18
650	4·50	4·70	4·20	4·60	4·24
700	5·70	6·00	5·40	5.80	5·36
750	7·20	5·90	6·85	7·30	7·60
800	9·00	9·40	8·70	9·15	8·45
850	11·30	11·50	11·00	11·60	11·12
900	13·90	14·60	13·70	14·00	13·50
950	17·10	17·90	17·30	17·35	17·42
1000	21·00	22·25	21·31	21·90	21·40
1050	25·90	27·25	26·75	26·90	27·15
1100	31·90	34:10	32·80	33·50	32·30
1150	39·30	39·95	39·60	40·60	41·30
1200	46·20	51·35	48·30	48·70	49·30
1250	56·50	58·00	56·40	58·10	59·12

the material and upon the relation which exists between the stress and the twisting moment on the shaft. Of these m and n are obtained from the slopes of the logarithmic graphs. In the following table are given the mean values :—

TABLE II.—MEAN VALUES OF m, n, A AND B.

	Lower part.		Upper part.	
	m.	A.	n.	B.
Wrought iron, solid.......	0·296	403	0·254	451
Wrought iron, hollow	0·250	446	0·217	486
Mild steel, solid	0·356	368	0·259	465
Mild steel, hollow	0·285	424	0·231	490

Within the elastic limit the stress is proportional to the radius, and it follows that the maximum stress must be on the outside surface, and, consequently, the elastic limit must be reached and passed in the first place in a thin layer on the surface of the bar, and the thickness of this layer increases as the twisting moment becomes greater. Taking the material in this layer as plastic, and that material nearer the centre to be elastic, the total moment of resistance of the section made up of these two concentric parts will be :—

$$T = T_2 + T_1.$$

$$= \frac{\pi}{2} \cdot f_1 \cdot r^3 + \frac{2}{3} \cdot \pi \cdot f_1 \left(r^3 - r_0^3 \right),$$

r_0 being the radius at the outside of the elastic portion. But it is also known that $T_1 = \frac{\pi}{2}\phi \cdot r_0^4 \cdot G$, where ϕ is the angle of twist in circular measure per unit length of the shaft, and G is the shear modulus for the material in question. So the above may now be written :—

$$T = 2 \cdot \pi \left[\frac{\phi \cdot r^4 \cdot G}{2} + f_1 \frac{r^3 - r_0^3}{3} \right].$$

This latter expression is arrived at by St. Venant to represent the moment of resistance of a shaft under a torsional moment in which a portion of the material has been stressed beyond the yielding point while the remainder is left still elastic.

It will be seen that St. Venant assumes the material to be perfectly elastic within r_0, and to be quite plastic from r_0 to r. The former of these assumptions is a fair one to make, but it is doubtful whether it is quite reasonable to assume that the stress outside the elastic region is perfectly uniform as far as the outside surface. It would seem more probable that for some time after the elastic limit has been passed at the surface of the shaft there is a zone of material in which the law of variation of stress lies somewhere between $f \propto x$ and f = constant. As the shaft is twisted further and further, there will come a time when there is practically no elastic portion left, and the whole section will be more or less plastic. Perfect plasticity will be attained first at the surface, and will gradually penetrate inwards as the twisting moment is increased and the shaft becomes more strained.

The information to be gained from the above is not sufficiently complete to establish a general law, but it is possible to arrive at the following distinct conclusions :—

1. There appear to be three stages or periods in the life of a shaft when tested to destruction. These are, the elastic stage; what may be called the semi-plastic stage; and, lastly, the plastic stage. The logarithmic plotting of shear stress and angular strain during the elastic period would lead to a line inclined to the zero line at an angle of 45 deg.

2. The change from the first to the second change is not sudden, but takes place gradually.

3. During the second stage the index for the angular strain, from being unity in the elastic stage, is decreased to a value which varies from 0·25 to 0·35.

4. During the third and last stage the index is again smaller than in stage 2, being from 0·217 to 0·259.

5. It is very probable that at the end of the third stage the shear stress in the metal is sensibly uniform. This is shown to be the case by calculating the ultimate stress from the formulas which are

deduced on the assumption that the stress is uniform, and comparing these calculated stresses with the stresses obtained from direct shearing tests on the same material. These values are seen to agree very nearly. The figures are as follow :—

Kind of shaft.	Calculated stress, lb. per square inch.	Direct shear stress, lb. per square inch.
Wrought iron, solid........	48,500	45,500
Wrought iron, hollow......	45,609	45,500
Mild steel, solid	48,900	50,200
Mild steel, hollow	51,800	50,200

6. The change from the second to the third stage is not abrupt, but takes place gradually.

7. The change from semi-plasticity to plasticity takes place when the material has been distorted through an angle of about 11 or 12 deg.

8. As the logarithmic plotting gives a continuous straight line from this "change point" to the end of the loading, it may be assumed that the condition of the material as regards variation of stress is the same throughout the third stage.

9. On the assumption that the shear stress is constant during the third and last stage of a torsion experiment, the following equations, giving a relation between f and a, are obtained :—

$$\text{Wrought iron, solid} \quad f = 16,700 \; a^{0.254}$$

$$\text{Wrought iron, hollow,} \quad f = 20,000 \; a^{0.217}$$

$$\text{Mild steel, solid} \quad f = 17,200 \; a^{0.259}$$

$$\text{Mild steel, hollow} \quad f = 20,200 \; a^{0.231}$$

Influence of the final angle of distortion on the cutting action of turning tools. In a paper read before the Royal Society in 1881, Mr. A. Mallock discusses, among other things, the nature of the action which takes place when a turning or other similar tool removes material from the piece which is being operated upon, and he shows that the usual form of shaving as it leaves the tool consists of a series of parallel slices, each one being successively partially sheared along the parallel lines, there being sufficient adhesion between the slices to allow them to come away from the work as one continuous shaving. The fact of a slice beginning to shear depends upon the ultimate angle of distortion for the material in question.

FINAL ANGLES OF DISTORTION.

Material.	Wrought iron, solid.	Wrought iron, hollow.	Mild steel, solid.	Mild steel, hollow.
Angles of distortion...... ⎫ Degrees..................... ⎭	60·39 60·55 63·83 62·38 61·35	44·60 42·47 40·90 50·92 47·62	60·90 59·10 59·00 55·41 53·75	56·50 58·00 56·40 58·10 59·12
Mean	61·70	45·30	57·63	57·62

These agree very nearly with the actual angles of shaving slices.

TESTS ON BRICKWORK PIERS. W. C. POPPLEWELL. The "Journal of the Institute of Sanitary Engineers," December, 1906. Results of tests of five brickwork piers, 1½ feet square and 3 feet high, made of Accrington bricks and Portland cement mortar. Tested six weeks after building.

Mortar used: Sand. —— Cement.	Proport'nal limit, last time of loading.	First Crack.	Crushing.	Ratio— Strength of brick.	Crushing strength of mortar.	
				Strength of brickwork.	At seven weeks.	At twenty weeks.
	Tons per square foot.				Tons per square foot.	
1—1	85	97	125	3·1	79	98
2—1	80	91	159	2·4	32	51
3—1	78	79	125	3·1	27	28
4—1	72	90	116	3·3	20	24
5—1	72	69	125	3.1	16	18

The above figures are given as being supplementary to those contained in the author's paper printed in the " Journal," vol. 1, part 2.

REPORT OF INVESTIGATION MADE IN THE MATERIALS TESTING LABORATORY INTO SOME OF THE PROPERTIES OF COPPER TROLLEY WIRE AND TRAM RAIL JOINTS SUPPLIED BY THE MANCHESTER CORPORATION TRAMWAYS DEPARTMENT. W. C. POPPLEWELL. The object of these experiments was to find out how and to what extent the dimensions and strength properties of wires had been affected by annealing, by the wear of the trolley on a straight run, and by the soldering of the wires to the suspending ears. Four conditions of the wire were taken account of. Of these, A was a length of new wire which had been softened by heating and quenching; B, wire in its hard draw state as used; C, wire which had been soldered under the suspension ear and had been in use in the streets of Manchester

for about two years; while D, plain hard-drawn wire which had been in use on a straight run for the same time. The results of the experiments described in the paper are summarised in the following table :—

Specimen.	A.	B.	C.	D.
Initial diameter, inches.......	0·403	0.404	0·365—0·396	0·374—0·399
„ area of section, sq. in.	0·127	0·128	0·114	0·117
Maximum load, tons	1·80	2·90	2·50	2·60
Stress at maximum load, tons per sq. in.	14·10	22·60	21·90	22·20
Elongation at maximum load, per cent...............	35·20	2·80	1·54	1·49
Elongation after rupture, per cent......................	45·80	5·70	4·06	3·50
Limit of proportionality, tons per sq. in. (about)...	...	7·80	7·80	6·80
Modulus of elasticity, lbs. per sq. in.	...	16,000,000	16,800,000	17,500,000

In the case of C and D it will be seen that a considerable reduction of area had taken place owing to the wear of the trolley wheel, amounting to some 9 per cent. There was practically no decrease in strength after two years either in the plain wire or, what is surprising, in the soldered portion. In the paper all the detailed measurements are given, and a diagram of the plotted load-strain curves is shown. The latter part of this paper is devoted to a description of the results of deflection experiments on three tram rail joints. Of these the first is a solid rail, the second a fishplate joint, and the third a "weldite" joint. The solid rail is best both in maximum strength and stiffness; the weldite is just about as stiff, but has a lower maximum; while the fishplate is much below the others both in stiffness and in the maximum load sustained.

A SIMPLE FORM OF VERNIER MICROSCOPE. ARTHUR ADAMSON. "Memoirs of the Manchester Literary and Philosophical Society," December 16, 1902. This apparatus is specially devised to be used by the elementary student who wishes to calibrate or determine the bore of a glass tube by measuring the length of a mercury thread within it. Two parallel scales, divided in tenths of inches and centimetres respectively, are fixed horizontally on a wooden base, between them being a longitudinal V-shaped groove in which the tube to be calibrated rests. A circular hole is cut through the base at one part of the groove, and a spring clamp is arranged for holding in this hole a piece of tube of fairly wide bore, with its axis vertical, so that its diameter may be measured directly.

The arrangement for reading is similar to the cursor used with a slide-rule. A thin plate of transparent celluloid is fixed in a metal frame which can slide over the scales and groove. On the under surface of the celluloid is marked a fine transverse straight line, which is adjusted, by sliding the frame, so as to be exactly over the end of the mercury thread to be measured. A short strip of mirror glass is fixed to the under surface of the celluloid, so that parallax errors may be avoided. The readings on the scales are taken by the aid of two verniers attached to the celluloid. The observations are made through a reading lens carried by the sliding frame. A vertical pillar attached to the frame supports the lens, and also, at a suitable height above it, a horizontal metal disc with a narrow slot cut in it. The slot, the centre of the lens and the cross line on the celluloid are all in one vertical plane, so that if the cross line be observed through the slot and lens, all parallax errors are avoided.

NOTES ON ELECTRICAL CONDUCTIVITY. WM. BROWNING (Student). "Proceedings of the Institution of Electrical Engineers," 1906, part 180, vol. 37. The notes deal chiefly with conductivities of contacts, the values of which are expressed in terms of amperes per square inch, per millivolt of potential across the contact. The conductivity of the contact, between two brass discs in air, was found to vary almost directly as the mechanical pressure between them, up to a certain critical pressure, after which any further increase of pressure appeared to have no effect. The critical pressure was shown to depend upon two factors—the hardness of the metal, and the nature of the surface of the contact, whether rough or smooth. Tinfoil was only useful in increasing the conductivity of a contact, when the surfaces were rough. The critical pressures examined lay between the limits of 17 lbs. per square inch for tinfoil, and 35 lbs. per square inch for brass. Both resin oil and vaseline increased the conductivity in about the same proportion for pressures above the critical pressure, both when present in large quantities, before the contacts came together, and when present only as a thin film such as can be put on by a greasy rag. It was

supposed that they had a cleansing effect, and prevented any oxide forming on the surfaces, and further that the resistance was decreased by the filling up of the minute valleys of the surfaces with oil, which had a finite resistance, while the air which previously filled the spaces, had practically an infinite resistance. Their influences on the critical pressure were not similar. Resin oil lowered it 50%, while vaseline lowered it only by 10%.

The comparison of the relation between conductivity and mechanical pressure for the two methods of applying the oil, as shown by a set of curves, showed a marked difference in the two cases for pressures below the critical pressure. When the oil, or vaseline, was present in the larger quantity the increase of conductivity was greater during the latter part of the curves, from one-half to full critical pressure, than for the first half; while for the slightly oiled contact the rate of increase was approximately uniform, and in form was similar to the dry contact curves. It was shown that in the case of laminated switches, the laminations, as they spread out over the surface of the contact as the switch is closed, often tilt so that the whole of the surface of the edge of each lamination is not in contact. This had the effect of decreasing the conductivity due to a reduction of the efficiency of the contact, which was only partly made up by the increase of conductivity due to the increasing pressure. The notes concluded with a reference to the effect which the temperature of annealing has on the final conductivity of a copper wire.

FURTHER NOTES ON ELECTRICAL CONDUCTIVITY; STATIONARY CONTACTS, OILED AND DRY. WILLIAM BROWNING. "Proceedings of the Institution of Electrical Engineers," part 186, vol. 39. The paper contains the results of further research on the above subject, and its objects were :—(1) The examination of the factors which determine the pressure at which the conductivity of a contact in oil assumes a constant value for constant current density and temperature; (2) the relation between current density and conductivity; (3) the relation between temperature and conductivity; (4) to compare the above with a dry contact. For the oiled contact experiments a resin switch oil, of which a complete analysis was given, was used, and this was compared at times with other oils and media.

The factors which determine the critical pressure of a contact in oil. It was found that, while obtaining values of conductivity at constant current and temperature for varying pressures, the conductivity did not immediately take up a steady value after a change in pressure, between the limits of zero and about three-quarters of the critical pressure. The curves of increasing and decreasing pressures enclosed a loop, the area of which was found to have the dimensions of an amount of work. This was supposed to be the amount of work done against the viscosity of the oil, from

which it was deduced that the viscosity did not influence the critical pressure. When different media were employed, whose surface tensions could be compared, it was found that the value of the critical pressure varied directly as the surface tension, but the exact relation was not investigated. The critical pressure was independent of the area of contact.

Relation between current density and conductivity. Three sets of readings of conductivity for constant pressures of 6·25, 18·25 and 30·25 lbs. per square inch were obtained for varying current densities. The readings were afterwards corrected for temperature. The conductivity decreased with increased current density, and the rate varied with the value of the pressure, that is with the thickness of the film. From a minimum, with the thickest film, the rate gradually increased to a maximum, for a pressure greater than the critical pressure, where the film was in its limiting condition for the temperature to which the curves were corrected.

Relation between temperature and conductivity. The conductivity was found to increase with temperature, and the rate of increase varied with the conditions of current density and pressure. For cases below the critical pressure, which showed a marked difference from those above that limit, it was shown that the decrease of the surface tension, due to the rise of temperature, caused a lowering of the value of the critical pressure, and that this corresponded to a displacement of the pressure-conductivity curve towards the axis of conductivity. As this would not have any effect on the values of conductivity for pressures above the critical pressure, it was concluded that there were other factors not investigated which were also changing.

Comparison of the characteristics of a dry contact with those of an oiled contact. The results of several experiments with a dry contact were described, which showed that the value of the conductivity was modified by the oxidation of the surfaces in contact. With a freshly cleaned contact the conductivity gradually decreased with time, either with or without the passing of current, until a point was reached when the oxidation appeared to cease. With the contact in this condition the following relations were established :—That for low values of current density the conductivity decreased rapidly with decreasing current density; that there was no variation of conductivity with temperature. Some direct comparisons were made between the conductivities of two contacts, a plain copper and a laminated brass, when measured, first dry and then under the surface of resin oil. In each case the presence of the oil increased the conductivity about 40%.

ELECTRICITY AND MATTER, WITH SOME ACCOUNT OF RADIATIONS. L. H. A. CARR. "Journal of the Institution of Electrical Engineers," vol. 41. (Awarded Premium.) When dealing

with power we have been accustomed to consider amperes as the more fundamental unit, and coulombs as merely a product of amperes and seconds. Electromagnetic phenomena, too, have been considered in relation to the ampere. That is, 1 ampere has a certain definite magnetic effect. (I purposely use the practical and not the absolute units for discussion here, so as the better to fix our ideas.) But a coulomb we know to be a certain definite quantity of electricity, just a certain number of corpuscles, whether at rest or in motion. An ampere is just the rate of flow, that is, the passage of electricity at the rate of 1 coulomb or x corpuscles every second. That is, coulombs exactly correspond to gallons of water flowing in a pipe, coulombs being composed of x corpuscles in the same way that a gallon of water is composed of x molecules, and amperes directly correspond to flow in gallons per second. It must then be established in the mind that the magnetic effects are not due merely to the passage of something indefinite, which we call "an ampere," but are due to the moving coulombs, and are, in fact, dependent on the momentum of the coulomb, that is to say, the momentum of all the corpuscles together, or the sum of the momentums of the individual corpuscles.

From this point of view it is easy to see why a moving sphere carrying a charge should give rise to electromagnetic phenomena. Also a corpuscle in motion will give rise to electromagnetic effects. If we imagine the magnetic effect of a conductor not to be due to 1 ampere, but to a flow of 1 coulomb per second, we get a better idea of the cause of this magnetisation. For if a flow of 1 coulomb per second causes a certain magnetic effect, then since that coulomb is composed of a number of corpuscles (8.7×10^{18}, to be exact), then a small proportion of that magnetic effect must be due to each of those corpuscles when in motion, so that any corpuscle in motion produces a magnetic field around it as it travels. Consider unit length of a conductor of uniform cross-sectional area. We will assume the simplest case of an electric current—namely, where it is simply the steady uninterrupted flow of corpuscles from the negative to the positive. Now unit length (1 cm.) of this conductor will have a certain magnetic effect, or magneto-motive force M. Then let—

$A =$ cross-sectional area of conductor in square centimetres.

$v =$ the average velocity of the corpuscles.

$m =$ the individual mass of each corpuscle—apparent mass, perhaps, I should say.

$e =$ electrical charge (in coulombs) of each corpuscle.

$\Delta =$ the density or number of corpuscles per cubic centimetre (the number of free corpuscles per cubic centimetre is constant for the same (solid) substance).

$c =$ current in corpuscles per second.

$C =$ current in coulombs per second—that is, in *amperes*,

$$C = \frac{c}{K} \text{ where K equals } 8.7 \times 10^{18}$$

hence—
$$e = \frac{1}{K}.$$

Then M, the M.M.F., is proportional to the sum of the electrical momentums of all the corpuscles in 1 cm. length.

M ∝ the whole charge of the corpuscles per unit length × their velocity.

$$M \propto (A \times 1 \times \Delta) \times e \times v$$
$$\propto \frac{A \, \Delta \, v}{K}.$$

Now v, the velocity, is such that c the current $= v \times$ corpuscles per unit length in corpuscles per second, that is—

$$c = v \times (A \times 1 \times \Delta),$$

and—
$$v = \frac{c}{A\Delta}.$$

Substituting in the above equation this value for v we get—

$$M \propto \frac{A\Delta}{K} \times \frac{c}{A\Delta};$$

that is—
$$M \propto \frac{c}{K}$$

$$M = \text{a constant} \times C,$$

or the magneto-motive force per unit length of conductor varies merely as C the current in coulombs per second, or amperes as we usually term it. This, of course, we know to be true. So although the magnetic effect due to any one corpuscle varies as its speed, and is hence dependent on the area of the conductor and the density of corpuscles, yet the total magnetic force is always the same as long as a quantity of 1 coulomb passes any given plane per second.

The conduction of electricity in a solid is, however, not purely a steady passage of corpuscles, as we have assumed above, but is really a series of exchanges. In an ordinary solid at rest (and here I am talking of conductors, not insulators) we think that corpuscles are constantly straying from their atoms, and after a short journey in the metal, finding a home in another atom, one of whose corpuscles has also gone off on a roaming expedition. Still, however, as the sum total of all the corpuscles is constant, and so is the sum total of the positive electrification, the piece of metal remains uncharged. Now if we apply an E.M.F. to the ends of the piece of metal, these atoms become polarised as it were, and all the corpuscles leave the atoms in the same direction and jump into the next one in the chain, so that there is a transference of electricity from the negative pole, and hence this would speedily become positively electrified were it

not supplied with corpuscles from the source of supply of the E.M.F. The corpuscles have a very short, free path between the atoms and move along it with a very high velocity.

The conduction of current in liquids takes place in quite a different manner, and is by means of dissociated atoms or ions. These ions move extremely slowly, so that for every ampere or coulomb per second which passes a given place, since the velocity of the electricity is slow the number of corpuscles in the solution must be large. It will be remembered that I have referred to the expression—

$$C = vA\,\Delta,$$

obviously since v is exceedingly small (being but a fraction of a centimetre per second) $A \times \Delta$ must be larger—as a matter of fact both A and Δ are larger, for with copper 1,000 amperes per square inch is quite common, while with an electrolyte only a few amperes per square inch is the normal density, and were one to apply such a voltage that would give a density of 1,000 amperes per square inch to an electrolyte (worked out from Ohm's law) the current would arc across through the electrolyte.

The extreme slowness of the corpuscles in an electrolyte is, of course, due to the fact that they are not free corpuscles, but are tied on to the large mass of an atom, forming an ion which they have to drag about with them. When an ion (either positive or negative) arrives at the electrode it yields up its corpuscle (if negative), or takes in one (if positive), and becomes the normal atom or collection of atoms; thus if a hydrogen ion is under consideration, it will become a hydrogen atom, and united mechanically with other hydrogen atoms formed in a similar manner, forms a bubble of hydrogen gas which escapes into the air. If it is an SO_4 ion (as in a solution of sulphuric acid) it will either attack the electrode when it is de-ionised, if of lead or other corrosive material, or else decompose a water molecule forming sulphuric acid and liberating an oxygen atom, which will, when enough atoms have collected, be given off as a bubble of gas.

Though the magnetic effect of each corpuscle in a liquid is far less than that of one in a metal conductor, its velocity being much less, yet the total magnetic effect will, as has previously been explained, be exactly the same if the same number of coulombs per second be flowing. That this is actually so I have experimentally proved. The liquid conductor was a solution of common washing soda in a wooden trough 2 in. deep × 2 in wide × 24 in. long; above this was placed an ordinary compass, and above this at a distance from it equal to that of the centre of the liquid conductor was placed a copper wire. The whole arrangement was placed in the magnetic meridian, so that when undeflected the needle pointed along the trough. The needle was deflected equally whether a current of a certain number of amperes was sent either through the liquid or through the copper wire—only, of course, in opposite directions—as it was over one

conductor and below the other. The object of having such a length of liquid conductor was to eliminate any effect due to the leading-in metallic conductors, which was, of course, negligible at the centre of the trough. Conduction in gases is also by means of ions, but is much freer than with liquids as the molecules of a gas not being packed anything like as closely as those of a liquid, progress of the ion is much easier. In a rarefied gas, as in a vacuum tube, some of the current may be in the shape of free corpuscles themselves.

PRESSURE DROP IN ALTERNATORS. W. CRAMP. "Electrical Engineer," August 12, 1904. From Ferraris' well-known theorem for the resolution of an alternating magnetic field into two equal but oppositely rotating fields, and from the principles of the semicircle diagram for polyphase motors, the author develops a graphical method of determining the pressure drop at the terminals of an alternator for given load conditions when once the open-circuit and short-circuit characteristics of the machine are known. The method outlined resolves itself into a semicircle locus diagram for the whole circuit, in which lines representing the potential difference at various points of the circuit are drawn. The correction necessary for saturation of the iron circuit is considered, and the methods are checked by experiments on a small machine. Finally a graphical method of predicting the change in characteristic due to a change of frequency is given, and this is checked by an actual experiment.

THE OZONE PROCESS OF FLOUR BLEACHING. W. CRAMP. "Milling," December 23, 1905. This paper describes the apparatus manufactured by the Ozonised Oxygen Company for the bleaching and sterilising of flour. The chemical aspect of the question was discussed at the meeting of the British Association in York on August 24, 1906, and this account simply gives commercial details of the apparatus supplied, and of the methods of regulation.

THE ARTIFICIAL BLEACHING AND CONDITIONING OF FLOUR. W. CRAMP. "The National Association Review," July 13, 1906. This paper sets forth the various processes of flour bleaching which are actually commercially used. It gives a short account and explanation of the processes of :—(1) Alsop, (2) Andrews, (3) Leetham, (4) Mercier. These processes divide themselves into two groups, viz., those employing ozone, and those using no ozone. To the former belong Leetham and Mercier, and of these Leetham uses a mixture of ozone and oxides of nitrogen, while Mercier uses ozone mixed with chlorine. Andrews and Alsop, on the other hand, use peroxide of nitrogen, the former chemically prepared, the latter electrically. The effects of these gases on the flour are discussed, and accounts are given of experiments carried out to ascertain the effect upon the loaf produced. The experiments prove :—

1. That flour overtreated by the oxides of nitrogen processes shows itself in the loaf by the bluish look in the interstices.

2. That pure ozone does not, within the limits of the experiments, damage the flour at all, although it imparts to it the smell of ozone itself.

3. That the Leetham process is in results midway between that of Alsop and that of pure ozone.

The paper concludes with some hints as to the choice of process, and as to the question of advantage or otherwise of bleaching at all.

MAGNETIC LEAKAGE AND ITS EFFECT IN ELECTRICAL DESIGN. W. CRAMP. "Journal of the Institution of Electrical Engineers," vol. 38, page 540. This paper is divided into three sections. The first section deals with direct current machines, the second with alternators, the third with alternating current motors.

In the first section it is pointed out that since in multipolar machines beyond 200 k.w. the leakage factor only varies between 1·1 and 1·2, little saving in the cost of materials can be effected by adopting a special design having for its object the reduction of the leakage co-efficient. In small machines, on the other hand, the leakage factor may reach as large a value as 1·5, and consequently an appreciable improvement may be made by specially designing to avoid so large a factor. A design is described in which a reduction of the co-efficient from 1·35 to 1·1 results in considerable reduction of cost per kilowatt. In this machine the pole cores are made hollow and taper inwards, almost the entire space between them being filled up by the coils. It is also stated that such a construction leads to better results in commutation. Designs of this character are compared with machines which involve a single field coil only, such as the Lundell motor, which are said to produce what is called magnetisation of the armature. The following are conclusions reached :—

1. In machines up to 20 H.P. the leakage is sufficiently great to make it worth while to adopt special means to reduce it.

2. One of the best remedies is the placing of the field coils close to the armature and practically spanning the pole pitch.

3. A single coil may be adopted in place of the usual one coil per pole, but this is not as a rule economical.

4. The single coil will be more economical than the separate coils if the length of mean turn of the single coil is less than the length of mean turn of any one of the separate coils multiplied by half the number of poles.

5. Adopting either of these methods of field winding incidentally reduces both the weight of iron and the cost of the machine, and at the same time improves the commutation.

6. As the general result, therefore, smaller machines at a reduced cost can be built for the same output.

From these single coil machines the author passes to the construction of motors in which the flux is produced by a winding on the armature itself. Experiments are described carried out on a machine with a double commutator, in which one commutator is used for producing the field, and it is pointed out that such machines can hardly be of use for shunt motors on account of the expensive field winding. On the other hand, in the case of a series motor without field coils, the equivalent of a double winding on the armature may be obtained by displacing the brushes from the neutral point, and the ratio of armature to field ampere turns may be altered by brush movement. Such machines might be of use in certain special cases, but they would normally require a larger commutator and a smaller reactance voltage than the ordinary series motor.

Under the heading "Alternators" the author confines himself almost entirely to showing how use may be made of that leakage which must exist. From this point of view he describes a self-exciting and self-compounding alternator, of which many are in use, and which have been constructed since the year 1904, and therefore precede the "Heyland" machines more recently described. The machines illustrated are of the inductor type, and curves are given showing compensation for constant current and compensation for constant voltage.

In the last section of the paper the leakage factor of alternating current motors is dealt with, and corrections for Behn-Eschenberg's formula are suggested. Finally, the author describes a type of motor devised by himself.

The machine is really a type of series alternating current motor with a transformer combined, which allows of its use upon circuits of high voltage. The flux crossing the air gap is really a leakage flux produced by the primary and secondary windings of the transformer. In a table, this machine, the simple series motor, and the repulsion motor are all compared with a series motor in combination with transformers, from the points of view of (1) efficiency, (2) power factor, and (3) weight of active material.

SINGLE-PHASE MOTORS FOR TRACTION PURPOSES. W. CRAMP. "Electrical Review," August 9, 1907. The following paper is an account of tests carried out at the Municipal School of Technology upon the special form of motor outlined in the paper upon "Magnetic Leakage and its Effect in Electrical Design" ("Proceedings of the Institution of Electrical Engineers," 1907, part 183, vol. 38, page 512). The statements made in that paper led to a protracted discussion in the electrical press in January, February and March, 1907. In order to support the contentions of the author as to the characteristics of this motor, a special machine

was built, and tests of torque, speed, and current were taken to ascertain whether the circle diagram that has been published was sufficiently correct.

The main points of the motor are given in the abstract (on page 308) of the previous paper, but the accompanying diagram will make the principles of the machine clear.

Fig. 1.
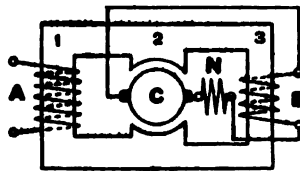
In this diagram (Fig. 1) A and B are the two limbs of the motor, C the armature. On the limb A is wound a coil connected to the supply mains. By transformer action the coil on the limb B supplies current to the armature C, which may or may not have a neutralising coil N in series with it. The main contentions were :—

1. That such a motor has characteristics of speed, torque, current, and voltage very similar to those of a series motor.

2. That with constant terminal voltage, the primary current may be expressed by a circle diagram very similar to that of the induction motor.

3. That as the speed rises the power-factor will rise, and there is no reason why the machine should not have, at full load, a power-factor as good as an induction motor.

Other contentions as to commutation and efficiency were also set forth. The tests taken were in two sets, one with the machine running as an ordinary series motor, the other arranged in the special form of the figure above. The results obtained clearly justify the use of the graphic construction as set forth in the Manchester paper, and prove all three contentions as mentioned above. The account includes the discussion of the various types of this motor that are possible, and a comparison of the weights for a given output.

ELECTRIC HEATING : ITS HISTORY & DEVELOPMENT.
A. E. JEPSON (Student). Read before the Manchester Students' Section of the Institution of Electrical Engineers, January 13, 1905. The manufacture of domestic electric heating appliances was begun in the United States of America about the year 1888, but the class of article put on the market was so ill adapted for the purpose that it gained a reputation for electric heating which has not yet been lived down. Within the last few years, however, much greater attention has been paid to the design and requirements of the apparatus, and the latter can now be obtained which has an efficiency of from 85% to 98%, depending upon the operation it may have been

made to perform. Radiators and convectors, of course, have an efficiency of 100%.

The main objection urged against the use of electricity for heating purposes is the high running cost, but there are many operations which can be performed cheaper than with gas or coal. Generally speaking, however, the price of electricity for heating will have to be reduced to 1d. per unit to compete successfully with gas at 3s. per 1,000 cubic feet. There are, however, many heating operations performed which would be impossible with any other method of heating. The practical systems in use at the present day employ resistances in lamp form, in metallo-ceramic bars, of wire suspended on insulators, or embedded in insulating powders or enamel. For small articles such as kettles, or sadirons, enamel is invariably used as the insulator, but unfortunately the insulation resistance of such enamel decreases enormously with an increase in temperature, and further, after a short time the enamel cracks off the body, and the generated heat not being carried away rapidly enough, the wire, which is run at a very high current density, fuses. A rather successful system employs thin films of platinum or gold, which are deposited on the enamelled bottom of cooking utensils, or upon thin sheets of mica which are fixed in frames and used as convectors, etc. Kettles, saucepans, etc., are wired for such a high watt consumption that the temperature of the heater would rise so high that it would melt the enamel if all the water boiled away. To prevent this, however, an ingenious device has been fixed to the bottom of these utensils, such that when the temperature of the heater rises above 100°C a fusible nut melts and breaks the circuit, and so saves the heater.

The larger pieces of apparatus are wired with several circuits, and these are arranged in such a manner that by means of switches or plugs the various circuits can be put in a series or parallel; this having the advantage that all the circuits in the heater are used, no matter what temperature is required. To prolong the life of sadirons, soldering irons, etc., which are required to be kept hot enough to be used immediately, and yet not consume the same current as when in use, stands are constructed to rest the articles on, having a resistance inside, which is switched in series with the circuit in the article immediately the latter is put out of the hand of the operator on to the stand. This has the effect of cutting down the current, and the heat generated in the resistance assists in keeping the article hot.

The arc also is used in the application of electricity for heating purposes, being adapted for reducing metals and oxides, etc., in the furnace, for filling up blowholes in castings, for large water boilers, and for large soldering irons where an intense heat is required in a comparatively small space. The heating effect of Foucault currents induced in metals by alternating currents is used

also for melting metals in a specially constructed furnace, and also for heating domestic appliances .

RELATION CONNECTING THICKNESS WITH DIELECTRIC STRENGTH. C. KINZBRUNNER. "Electrician," September 29 and October 6, 1905. These experiments were carried out under the working conditions specified in the previous extract. The author deduces the law of the variation of dielectric strength with the square root of the thickness of insulating material, the exception to this rule being Para rubber, for which the dielectric strength is practically proportional to the thickness. Laminating the material has no effect on the dielectric strength, the latter being the same for the laminated sheet as for a solid sheet of the same thickness. Where the material is subjected to mechanical strains, as for instance in bending round a surface of small radius, laminating the material is an advantage, and for slot insulation this is adopted in practice. The following table gives the values of the author and of other experimenters for the average dielectric strengths of layers of various materials 1 mm. thick (volts per mm.).

Material.	Arnold.	Rayner.	Wiener.	Baur.	Author.
Presspahn	7,400	5,000	6,000	—	4,600
Manila Paper	—	2,950	—	—	2,200
Ordinary Paper	5,500	—	8,000	5,000	1,450
Fibre	—	—	—	—	2,250
Varnished Paper	27,000	—	—	—	10,500
Red Rope Paper	19,000	10,500	—	—	9,400
Impregnated Paper	—	—	—	—	4,200
Varnished Linen	21,000	—	10,000	—	10,700
Empire Cloth	—	—	—	12,500	8,400
Leatheroid	5,600	—	—	—	3,050
Ebonite	31,500	—	—	—	28,500
Rubber	16,500	—	16,000	—	21,000
Guttapercha	7,700	—	—	—	19,000
Para	—	—	—	—	15,500

TESTING HIGH-TENSION INSULATING MATERIALS. C. KINZBRUNNER. "Electrician," September 8 and 15, 1905. These articles deal with a series of experiments undertaken to investigate the best conditions for the testing of insulating materials. In the first part is given a short description of the apparatus and instruments used in connection with the tests, and which form part of the equipment of the High-Tension Laboratory of the School. Presspahn was selected as the material for investigating the effect of the shape

of electrodes and the effect of the time of application of the electric pressure. The brass electrodes employed were : (1) pointed conical electrodes (angle of cone = 15°), (2) spherical electrodes of gradually increasing radii, and (3) flat electrodes with rounded edges. In using the flat electrodes the author found that the breakdown voltage (B.D.V.) is independent of the mechanical pressure exerted on the sheet of insulating material, provided that this pressure exceeds $\frac{1}{4}$ kilogram per square centimetre. The effect of frequency on the B.D.V. seemed to be small unless it was below 20 and above 75; the frequency throughout the experiments was 35. The "time curve" for insulating specimen giving the relation of B.D.V. and time of application of pressure shows that the material is capable of withstanding for a short time a much higher voltage than that which is sufficient to break it down if applied for a considerable period. The author terms the time required by the minimum B.D.V. the "time constant." The "time constant" increases with increasing radius of curvature of the electrodes and with the thickness of material. The deductions the author draws from the results of his experiments are : (a) to obtain the actual B.D.V. for an insulating material it is essential that it should be tested with a flat electrode; (b) since the B.D.V. is constant for flat electrodes of area greater than 2 sq. cm., electrodes of about 5 sq. cm. contact area are sufficient.

The author recommends a testing temperature of about 17°C, the material being tested in the normal state without any preliminary drying. With regard to the durations of time of a dielectric test, he thinks that it should be greater than the "time constant," and should be fixed according to the quality and thickness of the material. The following times may act as a guide for the materials used :—

Presspahn: 1 mm. thick, 4mins.; 2 mm., 6mins.; 3 mm., 8mins.

Paper (untreated): 0·1 mm. thick, $\frac{1}{2}$min.; 0·2 mm., 1min.; 0·3 mm., 1$\frac{1}{2}$min.; 0·5 mm., 2mins.

Varnished Paper (in one or several layers): 0·5 mm. thick, 2mins.; 1·5 mm., 3mins.; 3 mm., 5mins.; 5 mm., 8mins.

Varnished Linen (in one or several layers): 5mm. thick, 2mins.; 1·5 mm., 3mins.; 3mm., 5mins.; 5 mm., 8mins.

Rubber: 1 mm. thick, 1min.; 2 mm., 5mins.; 5 mm., 15mins.

Guttapercha: 1 mm. thick, 3mins.; 3 mm., 10mins.; 6 mm., 15mins.

Pure Para: 1·5 mm. thick, 5mins.; 3 mm., 8mins.

Ebonite: 0·5 mm. thick, 5mins.; 1 mm., 10mins.; 3 mm., 20mins.

The procedure for testing insulating materials, according to the author's views, is as follows :—The voltage should first be raised to the sparking point, in small steps, and at intervals of about 20

seconds. A new piece should then be taken, and the voltage should be reduced to about 70 to 80 per cent of the sparking or breakdown voltage; the time which elapses between the application of this reduced voltage and the ultimate breakdown (should such occur) is carefully noted. If this time is less than the time constant another test is made with a lower voltage. Should, on the other hand, the voltage be insufficient to cause a breakdown within an interval of time greater than the time constant, the test is repeated with an increased voltage.

NOTES ON A GRAPHICAL PROOF OF THE RULE FOR COMPARING RESISTANCES BY THE KELVIN DOUBLE BRIDGE. A. E. MOORE. " Electrical Engineer," December 28, 1906. The mathematical proofs of the rule for comparing resistances by the double bridge method are usually of a somewhat complex nature. With this difficulty in view, the writer devised the graphical proof given below.
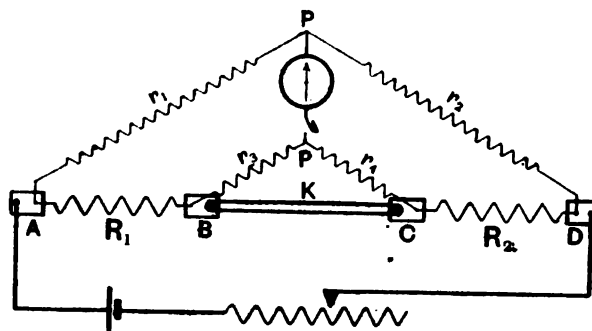
Fig 1.

Referring to Fig. 1, the condition for no current through the galvanometer on closing the key with

$$\frac{r_1}{r_2}=\frac{r_3}{r_4} \text{ is when } \frac{R_1}{R_2}=\frac{r_1}{r_2}=\frac{r_3}{r_4},$$

whence $$R_2=R_1\frac{r_2}{r_1}.$$

For the purpose of graphical proof the potential gradients in the resistances r_1, r_2, r_3, r_4 only need to be considered.

Case I. Let it be assumed that the resistance of r_1+r_2 equals that of r_3+r_4. This is generally the case in practice, and it gives the simplest solution. Let a potential diagram be constructed as shown in Fig. 2. Draw any straight line, A D, representing to some scale the resistance of r_1+r_2 (and r_3+r_4). At A and D erect perpendiculars and mark off the points A' and D' to represent the relative potentials

of the points A and D (Fig. 1) respectively. Join A′ D′. Then A′ D′ represents the potential gradient in $r_1 + r_2$. Mark off the points B′ and C′ in a similar manner to represent the relative potentials of the points B and C respectively. Join B′ C′. Then B′ C′ represents
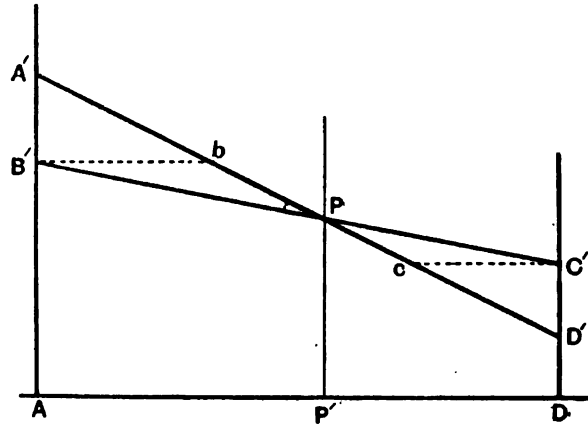
Fig. 2.

the potential gradient in $r_3 + r_4$. Now, since B is at a lower potential than A, and C is at a higher potential than D, B′ C′ will cross A′ D′ at a point P. Draw P P′ perpendicular to A D. P thus represents the two equipotential points on the gradients, and P′ the position of the equipotential points on the resistances. Further, it will also be clear that A′ B′ and C′ D′ represent the potential differences across R_1 and R_2 respectively. It is easily seen that

$$\frac{A' B'}{C' D'} = \frac{A P'}{P' D}.$$

therefore

$$\frac{\text{Drop of potential on } R_1}{\text{Drop of potential on } R_2} = \frac{r_1}{r_2} = \frac{r_3}{r_4}.$$

and since the current flowing through R_1 is equal to the current flowing through R_2,

$$\frac{\text{Drop of potential on } R_1}{\text{Drop of potential on } R_2} = \frac{\text{current} \times R_1}{\text{current} \times R_2} = \frac{R_1}{R_2}$$

$$\therefore \frac{R_1}{R_2} = \frac{r_1}{r_2} = \frac{r_3}{r_4}.$$

The above case is generally quite sufficient for the purpose of explanation, but while it is usual practice to employ equal resistances for r_1 and r_3, and also for r_2 and r_4, it is not essential that they should be equal so long as the ratio $\frac{r_1}{r_2}$ is always maintained

equal to the ratio $\frac{r_3}{r_4}$.

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Fig. 3 illustrates this point. Thus, if $r_3 + r_4$ be not equal to $r_1 + r_2$, let A D represent $r_1 + r_2$, and B C $r_3 + r_4$, such that

$$\frac{A\,P'}{P'\,D} = \frac{B\,P'}{P'\,C}, \quad i.e., \quad \frac{r_1}{r_2} = \frac{r_3}{r_4}.$$
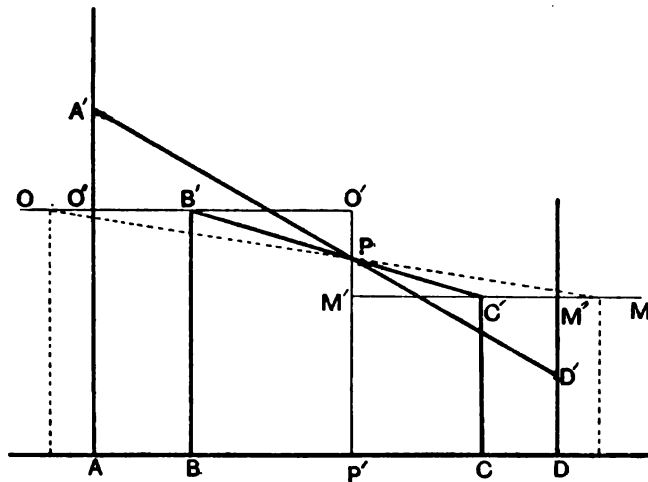
Fig. 3.

Let A', B', C', D' again represent the respective potentials of the points A, B, C, and D, and let O O' and M M' be drawn parallel to A D and passing through B' and C' respectively. Now, it will be obvious that any point on the line O O' will represent the potential of the point B, and similarly any point on M M' the potential of the point C. So that while B' C' represents the gradients in $r_3 + r_4$ for the particular case chosen, any line drawn between O O' and M M' passing through the point P will represent the gradient in $r_3 + r_4$, the position of such line depending on the resistance of $r_3 + r_4$. Again, the length A' O'' represents the potential difference between A and B (on R_1), and M'' D the potential difference between C and D (on R_2). It will also be clear from symmetry that

$$\frac{A'\,O''}{M''\,D} = \frac{A\,P'}{P'\,D} = \frac{B\,P'}{P'\,C}$$

i.e.,

$$\frac{R_1}{R_2} = \frac{r_1}{r_2} = \frac{r_3}{r_4}.$$

The dotted lines indicate a case when the resistance of $r_3 + r_4$ is greater than that of $r_1 + r_2$.

The following conclusions drawn from the illustrations are interesting :—The diagrams show that with a constant current through R_1

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and R_2 the sensitiveness of the bridge is independent of the resistance of the connecting strap, K (Fig. 1). Thus it will be obvious that the greater the resistance of K, the greater will be the differences of potential across A D and B C (Fig. 1) for a given current through R_1 and R_2. But the lengths A' B' and C' D' (Fig. 2) will remain constant, since they represent $R_1 \times$ current and $R_2 \times$ current respectively. Hence, if A remains at a constant potential, B will remain at a constant potential, while C and D will fall lower and lower in potential as the resistance of K is increased. Fig. 4 shows two cases—(1) when the resistance of K is
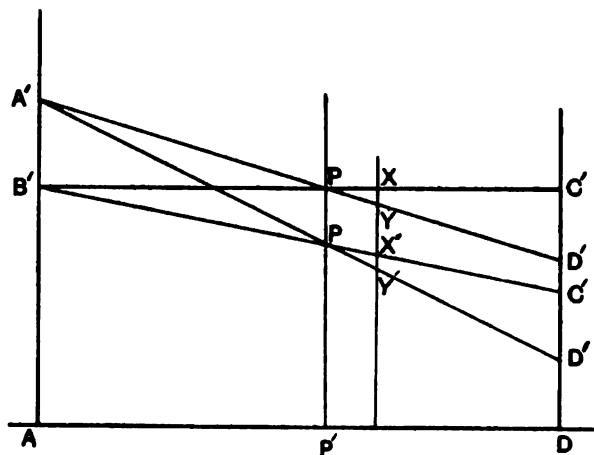
Fig. 4.

zero, and therefore, since there is no potential drop between B and C, the line B' C' is horizontal; and (2) when K is greater than zero, and hence there is a slope on B' C'. If now any vertical line be drawn from A D, it will at once be clear that the lengths $x\,y$ and $x'\,y'$, representing the potential differences available for the deflection of the galvanometer at that position, are the same in both cases. The lengths $x\,y$ and $x'\,y'$ will be seen to vary directly with the strength of the main current, and hence for a particular set of resistances the sensitiveness will also vary as the current. In a secondary sense, however, it follows that the sensitiveness may be diminished by increasing the resistance of K, since by so doing its current-carrying capacity may be diminished. In general, however, no increased sensitiveness will be produced by endeavouring to reduce the resistance of K to near zero; but when using the method for the comparison of low resistances, for which it is especially useful, it is well to remember that high resistance and bad contacts in such a connection are conducive to heating, and that heating may give rise to troublesome thermo E.M.F.'s.

The diagram Fig. 2 further shows that while any point on the line

B′ C′ has a point of equipotential on the part of A′ D′ between b and c, yet there can only be one point P on each line such that the ratio $\dfrac{B' P}{P C'} = \dfrac{A' P}{P D'}$—*i.e.*, the point where A′ D′ and B′ C′ intersect. For example, if two equipotential points other than P be chosen, one on B′ C′, and the other on b c, the ratio of the segments of the line B′ C′ would not be the same as the ratio of the segments of the line A′ D′. The position of the point P may of course lie anywhere between the two ordinates at A and D, depending on the ratio of the resistances R_1 and R_2. Thus, if the line A′ D′ be moved upwards without altering its "slope," the limit is reached when the point D′ coincides with the point C′—*i.e.*, when the resistance of R_2 is zero. The point P then also coincides with C′ and D′, or, if the resistance of R_1 be zero, then the points B′, A′, and P will coincide.

AN EXPERIMENT TO ILLUSTRATE THE PRINCIPLE OF THE HORN ARRESTER. A. E. MOORE. "Electrical Engineer," October 7, 1904. The author gives an account of some experiments illustrating the principle underlying the action of horn arresters. Frequently, the upward travel of the arc is ascribed to convection currents of air. In order to test the part played by convection, the author arranged two horn arresters, one pointing upwards and the other downwards. In each case the wires forming the "horns" were carried parallel to each other for a distance of 10 inches before diverging. When the horns were bridged some distance from their base by means of a carbon rod, which was then withdrawn so as to start an arc, the arc invariably travelled towards the divergent ends, upwards in one case, downwards in the other, thus showing that the effect was determined by electromagnetic action, and not by convection currents of air. If, however, the arc was started at the base of the horns, so that there was initially no electromagnetic action on it, its subsequent behaviour was uncertain, depending on the first accidental disturbance; sometimes it lingered at the base for a few seconds, sometimes it fused the horns off, sometimes it broke below the horns, and sometimes travelled upwards and broke. The author deduces from the above experiments the practical conclusion that horn arresters should be shaped thus > <, with the narrowest part, across which the discharge will take place, some little distance above the base. The arc will then certainly be forced upwards.

NOTES ON THE TESTING OF MULTI-RANGE AMMETERS AND VOLTMETERS, AND LOW-READING VOLTMETERS. A. E. MOORE. "Electrical Engineer," vol. 40, page 762, 1907. This article deals firstly with the method of recording the readings on a multi-range instrument, and the writer advocates taking down the actual deflections in divisions, and afterwards multiplying out

by the respective constants or multipliers. When this method of recording the readings is adopted, the best method of testing and expressing the accuracy of the instrument is to determine the constant by which the deflections must be multiplied in order to give true amperes or true volts.

In using the instrument, the recorded deflections are then multiplied by this determined constant instead of by the nominal multiplier for the particular range used. In the case of instruments in which the deflections on the scale are not quite proportional to the current through the instrument, a method is given for determining the correction for the scale, and in recording the readings in this case, the observed deflection is first corrected, and the corrected deflection then multiplied by the true constant. Various tables are given to illustrate the examples.

The second part of the article deals with the testing of low-reading or milli-voltmeters, with the potentiometer. The method consists in measuring by means of the potentiometer connected across a known standard resistance R_1, the current through a second standard R_2 of lower resistance, and across which the milli-voltmeter is connected. R_2 may be chosen of so low a resistance that the reduction in resistance brought about by connecting the milli-voltmeter in parallel with it, is negligibly small. The resistance of R_1 should be sufficiently high to give a large reading on the potentiometer when sufficient current is flowing through the circuit to produce the necessary deflection on the voltmeter.

NOTES ON THE STANDARDISATION OF FUSES. Alfred Schwartz. "Electrical Review," vol. 57, December 1, 1905. This article deals with the necessity for standardisation of fuses, from the point of view of convenience of replacement and the reduction of the fire risk. The matters in connection with which standardisation would be advantageous are stated to be : length of break, material, classification, rating and testing. It is suggested that the conditions and details of the following tests should be made standard :—Normal fusing current, short circuit, fusion with currents slightly in excess of the normal fusing current, temperature rise for enclosed fuse covers, insulation between parts. It is further recommended that standard types of contact and standard spacing between parts be adopted.

NOTES ON CONTINENTAL SYSTEMS OF FUSE STANDARDISATION. Alfred Schwartz. "Electrical Review," vol. 57, December 15, 1905. This article contains a detailed discussion of the German and French regulations for the construction and testing of fuses.

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NOTES ON THE AMERICAN SYSTEM OF FUSE STAN-DARDISATION. ALFRED SCHWARTZ. "Electrical Review," vol. 58, March 2, 1906. This article contains a critical resumé of the fuse standards and tests adopted by the Board of Underwriters and issued in the "National Electric Code" of 1905.

"FLEXIBLES," WITH NOTES ON THE TESTING OF RUBBER. ALFRED SCHWARTZ. "Journal of the Institution of Electrical Engineers," 1907, part 184, vol. 39. Awarded an Extra Premium. The introduction deals with the evolution of flexibles, the situations and classes of work in which they are employed and the fire risk attaching to their use. Summaries of reports of electrical fires from various causes are given, and the employment of a third wire laid up with the switch wires as a safety wire to ensure the blowing of the fuses is discussed. The relative conductivities of solid and stranded wires is then considered, and the ratio of the measured conductivity of the Cable Makers' Association stranded flexibles to the conductivity of a nominal equivalent solid conductor is shown to be slightly greater than unity.

There are four causes of weakness in flexible conductors which would appear to operate in actual practice : (1) Extension of the wires by bending when under small loads, (2) loss of tenacity due to increase of temperature at the lamp holder, (3) corrosion of the wires due to sulphur from the vulcanising compound, (4) corrosion of the wires due to chemical fumes in the air. With regard to (1), flexibles were bent many thousand times through a right angle at the lamp holder under a tension of three pounds, but an examination of the fractured ends showed that the diminution of section was quite local. A table is given showing the loss in tenacity of copper with increase of temperature, and measurements made on the temperatures attained in lampholders showed these to be much higher than is generally supposed, the highest temperatures recorded between the contact plates of the lamp being 329°F, and just above the cord grip 145°F, the temperature of the room at the time being 60°F. The temperature attained by contact plungers in BC holders for radiator lamps with the normal current flowing was found to be as high as 221°F, and with the contacts oxidised over 415°F. The heat of the lamp holder is conducted up into the insulation, and is undoubtedly the cause of many breakdowns. Experiments on the tensile strength of old flexibles insulated with pure rubber and with vulcanised rubber show that the action of the sulphur in the latter cases reduces the percentage extension of the wires at rupture from an average value of 19% in the case of wires insulated with pure rubber, to 8% in the case of vulcanised wires.

Section 3 of the paper is devoted to the heating of flexible conductors due to excessive currents, and curves are given showing the relation between temperature attained and time for flexibles with various types of insulation and various overload currents. These

are in every case less than the temperatures attained by bare wires under the same conditions. A further series of experiments was carried out with the same size of conductor in various finishes, but with currents up to 70 amperes, with a view to finding the kindling point of the insulation. The results show that vulcanised rubber insulation actually burst into flame only when the conductor fused, whereas flexibles insulated with pure rubber ignite before the wire fuses. The Cable Makers' Association vulcanised flexible 23/36 flamed in about seven minutes with a load of 40 amperes, and the same size wire insulated with pure rubber flamed in six minutes.

Section 4 deals with the insulation of flexibles, and reviews the various processes employed in the production of pure rubber strip, and of vulcanised rubber coverings, and gives vulcanisation curves for Para rubber at different temperatures. The oxidation and deterioration of rubber at high temperatures is then dealt with, and the effect of heat on the tensile strength of vulcanised rubber is then investigated, and the rate of deterioration at a given temperature is suggested as an index of the probable durability of the rubber in actual practice. The experiments of Shedd and Ingersol (" Physical Review," 1904) are referred to, and a number of curves are given showing the mechanical hysteresis of pure and vulcanised rubbers under various rates of loading. The hysteresis loop is suggested as a test for ascertaining the initial value of rubber insulation, a series of such curves being given to show how the character of the loop obtained under standard conditions varies with the quality of the rubber compound.

In dealing with the stretching of rubber, experiments were made to determine the effect of the dimensions of the test pieces in "cut" and "spread" sheet, and curves are given showing the relation between the stress in lbs. per square inch of the original area and the extension expressed as a percentage of the original length. Tests on completed flexibles are then considered, comprising (1) tensile strength, (2) bending on a counterweight fitting, (3) dielectric strength. Tables are given of the breaking loads of various sizes of flexibles, with and without the insulating coverings. These loads vary from 30 to 70 lbs.

In the bending tests an apparatus was arranged to simulate as nearly as possible working conditions. The flexible was drawn down by an attachment to a small motor and drawn up again by a counterweight once in each revolution of the motor. The motor, which was a small one, was fed through the flexible under test, and the revolutions counted until a breakage occurred in the conductor, when the motor stopped. The following are the particulars of the apparatus :—

Diameter of porcelain pulley .... $1\frac{1}{2}$ inches.
Length of pull............................. 6 „
Weight of counterweight .... $1\frac{3}{4}$ lbs.

The lowest recorded number of bends under these conditions was 9,560, and the highest 1,500,000, the specimen in the latter instance being special "gymp flexible," and it remained unbroken. Tests were then made by bending the flexibles through a right angle at a lamp holder, and sixty varieties of flexible were tested in the following way :—Five lamp holders were mounted in a line on a wooden batten with a short length of flexible depending from each, to which a 3 lb. weight was attached. The ends of the flexibles in the lamp holders were connected in series, and a small motor was fed through this circuit. The motor was arranged to rock the lamp holders through a right angle about the ends of the cord grips as centre once each revolution. When a conductor broke the motor stopped, and the reading was taken on the revolution counter attached to the motor. The flexibles were carefully inserted and treated as far as possible in the same way; the number of bends varied from about 1,500 to 155,000.

In the tests for dielectric strength, the samples were first subjected to the test conditions set out in the 1903 edition of the "Wiring Rules" issued by the Institution of Electrical Engineers, and were afterwards tested with a gradually increasing alternating voltage until they broke down. The breakdown voltage for vulcanised flexibles varied from 20,000 to 26,000 volts, and for flexibles insulated with pure rubber from 5,000 for single layer to 21,000 for two layers laid on in opposite directions.

The insulation of flexibles, while following in general the usual lines adopted for rubber cables, is subject to a rather different set of effects, in that the conductors of opposite polarity are in close contact throughout their length, and that the ratio of the amount of surface exposed to the air by the insulation to its thickness is larger in the case of most flexibles than for cables, and the maximum thickness of insulation to be dealt with is small.

Considering the features which it is desirable that the insulation should possess, and placing them in the order of their relative importance, we have (1) Durability, (2) High initial insulation resistance (3) Dielectric strength. The first is undoubtedly in the case of flexibles the most difficult to obtain, and also the most difficult to test for; while the second, although very generally considered of small importance, often affords a safer guide to the real character of the insulation than the high-voltage puncture test would do. The puncture test for dielectric strength, while usually specified for flexibles, is very rarely carried out in practice. A series of tests made by Clark ("Proceedings of the American Institution of Electrical Engineers," vol. 25, 1906, page 207), shows that neither the dielectric strength nor the initial insulation resistance of cables is an index of their durability as measured by the relative percentage deterioration in one year in the elastic limit of the material.

In order that the tests specified for an insulating material may have any real practical value it is essential that they should be simple in character, and easy to carry out. Viewed from this standpoint, any elaborate chemical analysis is out of the question, except in connection with large contracts; and we have to fall back upon the simpler chemical tests, such as the amount of acetone extract and the amount of ash, and the mechanical tests for tensile strength, and elongation, the physical test as to the behaviour in dry and moist heat, and the electrical tests as to dielectric strength and insulation resistance. We have by means of these tests to discriminate between insulation in which a certain minimum quantity of fine Para, Ceylon, or other good rubber has been employed and that into which recovered rubber and rubber substitutes and mineral matter too largely enter. Pure fine Para rubber contains about 1½ per cent of matter soluble in acetone, but during the process of vulcanisation this increases to from 3 per cent to 4·5 per cent. Oxidised oils and rubber substitutes are soluble in acetone, so that the percentage of acetone extract above that native to good vulcanised rubber is a guide to the purity of the rubber. In order to recognise the relation of the resinous extract obtained to the amount of indiarubber present, the percentage figures for these two constituents should always be calculated separately, so as to show the absolute percentage of resin contained in the indiarubber of the sample alone, and not in the whole contents of the compound.

The increase in the resinous extract only occurs in rubbers vulcanised by heat; cold vulcanised rubbers invariably show the normal percentages of resin. A consideration of a table giving the increase in resin on vulcanisation considerably discounts the value of the conclusions based on the acetone extract in respect of the rubber contained in an unknown sample. On the other hand, the amount of extract may be taken as a safe guide as to whether the sample has been manufactured from Para or not. The following specification has recently been agreed upon by the American Rubber Covered Wire Engineers' Association.

"For insulating compound containing not less than 30 per cent. by weight of fine dry Para rubber.

"The vulcanised rubber compound shall contain not more than 6 per cent. by weight of acetone extract. For this determination the acetone extraction shall be carried on for five hours in a Soxhlet extractor as improved by Dr. C. O. Weber.

"The rubber insulation shall be homogeneous in character, shall be placed concentrically about the conductor, and shall have a tensile strength of not less than 800 lbs. per square inch.

"A sample of vulcanised rubber compound not less than 4 inches in length shall be cut from the wire with a sharp knife held tangent to the copper. Marks shall be placed on the sample 2 inches apart. The sample shall then be stretched until the marks are 6 inches

apart and then immediately released; one minute after such release the marks shall not be over 2⅜ inches apart. The sample shall then be stretched until the marks are 9 inches apart before breaking. For the purpose of these tests care must be taken in cutting to obtain a proper sample, and the manufacturer shall not be responsible for results obtained from samples improperly cut."

The following elongation test is given by J. Langan as being intended principally for national code wire, and he considers that even by omitting all conditions as to rubber it would compel results that would be entirely reliable and satisfactory for all conditions of code use.

Elongation Test (Langan). The insulating material of every wire must stand an elongation test of stretching three times its length several times; that is, a piece 2 inches long must stretch to 6 inches and promptly return to within 20 per cent. of its original length. It must then stretch four times without break or rupture, and return to 25 per cent. of its original length.

The author has examined a number of specimens of flexibles purporting to be "new and old code wire," and has found them to be poor, hence the necessity for the addition of an elongation test to the tests specified in the national electric code, which are given in an appendix. A detailed examination of "code" wires is also given in an appendix.

The following tests are generally referred to as "Admiralty tests," but must not be taken as officially representing the Admiralty specifications :—

The "dry heat" test is carried out in an air bath and consists in exposing the samples for one hour to a temperature of 270°F. The "moist heat" test is carried out in a digester at 320°F., the samples having to withstand this temperature for three hours without injury. This test is purposed to disclose the presence of rubber substitutes by their saponification. Pure rubber will not stand these tests, as it melts.

The following elongation test is attributed to the Admiralty, and is certainly the best in common use at the present time : A 14-inch specimen to be clamped for 1 inch at the ends and stretched to double its length—i.e. 24 inches—to remain in this state for 24 hours without breaking, and on release after a further 24 hours the permanent elongation on the 12-inch length should not exceed 15 per cent.

The relative durability of vulcanised rubber and pure rubber flexibles in mills and other trying situations is a debateable point, and one on which the author hopes the discussion of this paper may throw further light. As things stand at present the Cable Makers' Association only make "C.M.A." flexibles in vulcanised rubber, and if engineers are to pin their faith to this material the author considers that the high-voltage tests should be made after immersion in water.

The immersion test could hardly be applied with advantage to pure rubber flexibles on account of the amount of water absorbed by this material. A consideration of the existing tests detailed above shows a great lack of uniformity and an undoubted want of a reliable "durability" test. The author suggests that a comparison with a standard hysteresis loop, together with a carefully specified stretching test after heating at 150°F. for a given time in air, would give much greater certainty as to the probable durability of the material than any of the tests referred to above. The author hopes to investigate this matter further in the near future, as such a test should be applicable to the thick coatings of large cables as well as to flexibles.

The thicknesses of insulation required by the regulations of various countries for flexibles is then dealt with, and a detailed description of the flexible wiring systems employed on the Continent is given. The attachments for flexibles are then considered, and the average loads at which slipping takes place in ceiling rose attachments and cord grips of various sorts are given. The various explanations advanced to account for the attraction of dust by flexibles are dealt with, and the paper is concluded with a full bibliography, and three appendices dealing with the American, French and German regulations for the installation of flexibles.

THE EXPERIMENTAL DETERMINATION OF LOSSES IN MOTORS. C. F. SMITH. "Proceedings of the Institution of Electrical Engineers," vol. 39, pages 437-477. In the first part of the paper the author deals with the losses occurring in continuous-current motors. After a detailed review of the various methods which have been suggested at different times for determining and analysing the stray power in continuous-current motors, the results of experiments carried out on a 3-H.P. motor are given, the method employed being one involving the use of a separate fly-wheel which could easily be coupled to, or uncoupled from, the motor. The acceleration and retardation curves, with a constant current maintained through the armature, supply the necessary data for calculating the losses. The author's experiments show a slight increase in the stray-power losses at full load.

A detachable fly-wheel is regarded by the author as furnishing a very convenient method of carrying out the complete test of a motor, and of analysing the losses; it is suggested that such a fly-wheel might well form a permanent part of the equipment of a test room. The second part of the paper deals with polyphase induction motors, and contains a very complete summary of all the more important methods of determining and separating the losses.

SINGLE-PHASE INDUCTION MOTOR DIAGRAMS. C. F. SMITH. "Mechanical Engineer," pages 870-872, December 21, 1907. In ordinary text-books the Heyland diagram as applied to the

single-phase induction motor is only represented by the approximate form, which fails to show the behaviour of the motor at all speeds. In the paper, a diagram is developed having a more complete form, and sufficient accuracy to show the behaviour of the motor at all speeds without serious error. The usual approximate diagram is given and compared with the new and more complete form. It is shown that for speeds near to synchronism the divergence between the two forms is small, while for low speeds the approximate form gives misleading results, while the new diagram still maintains its accuracy.

FLOUR BLEACHING. JAS. GRANT. Read at the Conference of Master Bakers and Confectioners, 1907. The first portion of the paper deals with the composition of the wheat caryopsis, especial attention being directed to the bran layers, which consist of two parts, the pericarp and testa. The former is built up of the epicarp, mesocarp, cross cells, and the so-called tube cells; while the latter (testa) is composed of the spermoderm, containing the pigmentum and the perisperm. During the milling these bran-forming substances are broken up, and the minute particles not taken out by the silks tend to give the flour a greyish or brownish-grey colour, thus spoiling its appearance. Chemically, the pigment is a benzene derivative containing several nitrogen groups in the ring. The objects of bleaching are, if possible, to destroy this colouring matter and at the same time to increase the strength of the flour. The only other constituent of the flour to be bleached is the natural oil contained in the germ.

The various patents bearing on the subject are reviewed, and several of the processes described. The latter part of the paper is devoted to the effects of flour bleaching as shown by an exhaustive series of experiments as carried out in the Bakery of this School. These demonstrate that medium and low-grade flours are improved to a very considerable extent. They give an increased yield of bread, a bolder-looking loaf, a brighter bloom, a whiter crumb, a strengthened gluten, and a partially sterilised flour, thus adding to its keeping properties. A bleaching treatment only slightly prolonged absolutely spoils the flour for all purposes.

TOWN TYPES OF BREAD, WITH ESPECIAL REFERENCE TO MANCHESTER BREAD. JAS. GRANT. ("Bakers' Magazine," 1907.) Bread may be defined as the baked product of any cereal meal and water, irrespective of any other added ingredients. The great bulk of Manchester bread is manufactured from flours milled from near the middle of the wheat caryopsis, hence, although it may be creamy-white or dead-white, it is somewhat deficient in such food-forming materials as proteids, fats, and phosphates. Three qualities of bread are made from many different grades of flours, but

even the lowest grade is much better than the bread supplied in country districts and small towns. The chief types in common use are :—(1) Set breads, including ordinary tin, long and short split tin, cauliflower tin, pan bread, box tin, and sandwich bread; (2) crusty bread, including cottage, bricks, Brunswicks, Coburgs, milk breads, and Viennas; (3) proprietary breads almost innumerable, and special breads. Manufacturing processes, quantities and temperatures are accurately described, the chemistry of the subject is fully discussed, and many analyses and illustrations are given. The analytical results cover a period of over two years, and go to prove that the composition of the best white bread is :—Carbohydrates 52·40%, water 39·64%, proteids 6·80%, ash 0·60%, fats 0·42%, and acidity calculated to lactic acid 0·14%. Generally, the moisture in Manchester bread varies between 33% and 46%, ash or mineral salts 0·38% and 1·75%, acidity 0·114% and 0·58%.

In brown breads the figures are :—Moisture between 38% and 45%, ash 0·77% and 1·57%, and acidity 0·18% and 0·42%. Methods of judging breads are fully described, and certain severe criticisms passed, especially in connection with the flavour and aroma of much of the trade bread. Under the head "Adulterations," it is shown that for over two years in which our "staff of life" had been under surveillance only slight adulterations, mainly due to the use of bread improvers, had been noticed. The worst that could be said was that some of the flours in common use were rather too strongly bleached. The bread improvers, whilst whitening the crumb of the loaf, were proved to be the chief cause of the rapid drying when a cut surface was exposed to the air. To summarise, after taking all factors into consideration, it can be shown that the popular tin bread in Manchester is of excellent quality, fairly nutritious and assimilable, and so cheap as to be within the reach of all to purchase the best quality.

BACTERIAL CONTAMINATION OF BREAD. JAS. GRANT. Read at a meeting of the Manchester Bakery Students' Society, 1908. It is well known that wheats and other cereals, owing to the deep furrow down the centre of the ventral side of the caryopsis, and to the hairs at the top, are liable to cause bacterial diseases in our food supplies. Although washed several times in the preparation for milling, it has not been found possible to get rid of the whole of the bacteria. Fruits equally with cereals are liable to this contamination. Flour, then, is not germ-free. It is claimed by millers who bleach their flours (vide the previous abstract) that the process renders it sterile. Research has shown that this claim is justified only to a limited extent. The study of bread-making during the last five or six years has brought a number of very interesting cases under the author's observation, but the one that caused the deepest impression was that of disease in sandwich bread. In this particular case, after a few days' keeping, a peculiar formation, resulting in an

oblong narrow hole, was developed in the centre of the loaf, and running in the direction of the length. All around the low flat hole the crumb had a dull sodden appearance, and this was accompanied by a very unpleasant odour. From general observations of the loaf one readily came to the conclusion that the disease was due to. bacterial action. Many series of experiments were carried out, some producing negative and others positive results. Ultimately we were able to isolate swarms of very minute oval-shaped non-mobile bacteria, and also many rod-shaped mobile organisms. The plate cultures yielded colonies, which rapidly increased in size, the disease spreading over the media in all directions. The cause of the disease was finally identified as belonging to the Proteus division of septic bacteria. These exist in most fertile soils, hence the research showed that the flour was produced from near the outer skin of the wheat caryopsis. In concluding, the author acknowledges the valuable assistance of his colleague in the Brewing School, Mr. F. G. Richards.

EXPERIMENTAL INVESTIGATION INTO THE PROCESS OF DYEING. JULIUS HÜBNER. "Transactions of the Chemical Society," vol. 91, 1907, page 1057. The present investigation into the process of dyeing has not been undertaken with a view simply to determine the proportions in which colouring matters, etc., are absorbed by various materials, as has been previously done, but it has also for its object a careful comparison of the behaviour of the different types of materials during and after the dyeing operation.

As a preliminary, further exact information was obtained as to the mode in which the absorption of colouring matters by fibrous materials is influenced by the degree of disintegration of the latter; the fibrous nature of the material used was not entirely destroyed in these experiments, but different series of observations were made with material of different mean length of fibre.

It is well known that fibres such as cotton, which have been converted into paper pulp by mechanical treatment in the presence of water, behave differently towards colouring matters than do the fibres in the original state. A quantity of material was prepared by boiling, etc., cotton yarn. Part of it was cut into pieces of about 2 inches in length, whilst the remainder was subjected to mechanical disintegration for various periods in the beating engine. The average length of fibre left in the beaten material at the end of the several periods mentioned was measured in the usual way, and the results are stated in Table I. For each of the absorption experiments the weight of cotton or pulp used corresponded to 20 grms. of absolutely dry fibres. The absorption tests were carried out with the basic colour Night-blue. It was found that equilibrium between dye solution and fibres was established in about 48 hours. Table I. shows the actual weight of dye absorbed by the 20 grams of dry material in

the various stages of disintegration and after different periods of immersion; it also states (in brackets) the proportion of the dye used which is absorbed by the material.

TABLE I.

GRAMS OF DYE ABSORBED.

Average length of fibre in mm.	Time of immersion in hours.	Original fibres.	1·5 hours' beating.	3 hours' beating.	4·5 hours' beating.	6 hours' beating.
		23·0	2·5	1·5	1·1	0·7
Cotton.............	1	0·0289 (0·1445)	0·1044 (0·522)	0·1137 (0·5685)	0·1168 (0·584)	0·1245 (0·6225)
	6	0·049 (0·245)	0·1177 (0·5885)	0·1183 (0·5915)	0·1184 (0·592)	0·1245 (0·6225)
	18	0·0551 (0·2755)	0·1183 (0·5915)	0·1183 (0.5915)	0·122 (0·61)	0·1245 (0·6225)
	72	0·644 (0·322)	0·1214 (0·607)	0·1269 (0·6345)	0·1294 (0·647)	0·1306 (0·653)
Average length of fibre in mm.		29·0	3·12	2·2	0·7	0·4
Wool	1	0·0305 (0·1525)	0·0351 (0·1755)	0·0382 (0·191)	0·0459 (0·2295)	0·049 (0·245)
	6	0·0366 (0·188)	0·0382 (0·191)	0·0413 (0·2065)	0·0462 (0·231)	0·0521 (0·2605)
	18	0·0413 (0·2065)	0·0428 (0·214)	0·0443 (0·2215)	0·047 (0·235)	0·0521 (0·2605)
	72	0·0521 (0·2605)	0·0521 (0·2605)	0·0521 (0·2605)	0·0521 (0·2605)	0·0521 (0·2605)
Percentage of water retained at 60°		3·24	2·13	2·33	1·47	1·51

It is noteworthy that the unbeaten cotton yarn shows a constantly increasing absorption during the 72 hours of immersion, whilst the most highly disintegrated material absorbs colouring matter very rapidly during the first hour of immersion, and but a very small amount of dye is taken up during the remaining 71 hours of immersion. It must thus be concluded that in the case of cotton the degree of subdivision of the fibre greatly influences both the total proportion of dye absorbed and the rate at which absorption occurs. It is remarkable that the most highly disintegrated material was found coloured to about the same depth of shade as the original yarn, although it had absorbed more than twice the proportion of colouring matter.

The fact that the wool fibre differs very materially from the cotton fibre as regards its structure and its dyeing properties made it of interest to study this fibre under similar conditions. A quantity of unbleached woollen rags (flannel) was scoured, washed, torn to pieces, and then disintegrated in the beating engine. In each experiment 10 grams of absolutely dry fibre were immersed at the ordinary temperature in 900 cc. of liquor containing 0·2 gram of Night-blue. The amount of colouring matter absorbed by 10 grams of wool, in the various degrees of disintegration and after different periods of immersion, is stated also in Table I. The results obtained with

disintegrated wool fibres differ very materially from those obtained with cotton. The amount of dye absorbed after 72 hours' immersion is the same whether the fibres are in the original state or in a very finely disintegrated condition. The original fibres absorb the colouring matter gradually, maximum absorption being obtained after between 18 and 72 hours of immersion; the finely disintegrated fibres (six hours' beating) behave quite differently in that maximum absorption is obtained after between one and six hours of immersion. The depth of shade of the dyed fibres after 72 hours' immersion is uniform throughout and independent of the degree of disintegration; this contrasts with the results obtained with cotton.

From this set of experiments it must be concluded that the degree of disintegration of the wool fibre influences the speed with which equilibrium is established as between fibre and dye, but does not influence the proportion of colouring matter ultimately absorbed. It might be suggested that the beating of the cotton or wool in contact with water produces some chemical change in the material; It was therefore desirable also to examine some fibrous material of simpler physical character than either cotton or wool, more especially with the view of ascertaining more directly whether the amount of fibrous surface exposed to the action of the dye-bath influences the proportion of dye absorbed. For this purpose artificial silk of two kinds, differing only in that they consisted of fibres of the average diameters 0·0299 mm. and 0·184 mm. respectively was used. Quantities of these two silks were cut into lengths of about 2 inches, and 10 grams of each (dry weight) were immersed for 72 hours in 750 cc. of solution containing 0·15 gram of Night-blue. The fine silk absorbed 0·0986 gram, and the coarse silk 0·0558 gram of colouring matter. It is thus clear that the finer silk, which exposes the larger surface, absorbs considerably more dye than the coarser material, and a direct indication is obtained that in the absorption of Night-blue by artificial silk the proportion taken up is roughly proportional to the surface exposed by the fibrous material.

Further confirmation of this result was obtained by studying the absorption of Night-blue by a chemically inert substance, namely, emery powder; two samples of levigated emery, the one very fine and the other much coarser, were used. One hundred grams of each kind were immersed for periods of 1, 6, 18 and 72 hours in 750 cc. of water containing 0·15 gram of Night-blue. The results were as follows :—

TABLE II.

GRAMS OF DYE ABSORBED.

Time of immersion in hours	1	6	18	72
Coarse emery	0·0081 (0·0587)	0·0167 (0·1113)	0·0263 (0·175)	0·05 (0·333)
Fine emery	0·05 (0·3333)	0·0618 (0·412)	0·09 (0·6)	0·09 (0·6)

The behaviour of the fine and coarse emery is clearly very similar in kind to that of the fine and coarse artificial silks, and also to that of the various grades of disintegrated cotton fibre. It is therefore concluded that the amount of surface exposed to the action of the dye solution greatly influences the proportion of dye absorbed, not only in the case of a material such as emery, which is certainly chemically inert, but also in that of cotton or artificial silk. In the above series of experiments a distinct analogy is traceable between the action of cotton and artificial silk and of emery powder on dye solutions. It seemed desirable further to extend the investigation for the purpose of ascertaining whether or not the indicated analogy has a real physical significance or not. Cotton, wool, silk, etc., were therefore dyed with a number of colouring matters typical of the different classes of coal-tar dyes, for the purpose of comparison with parallel trials carried out with such chemically inert substances as graphite, blood charcoal, China clay, etc. The colouring matter remaining in the dye bath was determined by titration in the cases of Night-blue and Naphthol-yellow S, and by the Dubosq colorimeter in all other cases.

Table III. gives the results obtained by immersing the materials named in the first column (10 grams dry weight) in 750 cc. of water containing 0˙25 gram (in the case of charcoal 3˙5 grams) of Night-blue. The numbers enclosed in brackets in this and the other tables state the proportions of colouring matter corresponding to the actual weights absorbed.

TABLE III.

GRAMS OF DYE ABSORBED.

	Cold.	Hot.	Cooled.
Cotton	0˙036 (0˙144)	0˙04 (0˙16)	0˙04 (0˙16)
China Clay ...	0˙1693 (0˙6772)	0˙17 (0˙68)	0˙172 (0˙688)
Graphite... ...	0˙2449 (0˙9796)	0˙2474 (0˙9896)	0˙249 (0˙996)
Wool	0˙05 (0˙2)	0˙23 (0˙92)	0˙2486 (0˙994)
Silk	0.236 (0˙944)	0˙246 (0˙984)	0˙249 (0˙996)
Charcoal... ...	3˙123 (0˙8923)	3˙495 (0˙9987)	3˙5 (1˙0)

It is concluded from the results given in Table III. that the absorption of the basic colouring matter Night-blue proceeds in a similar manner in every instance independently of whether animal or vegetable fibres or inorganic absorbents are used. After dyeing, all the materials were separated from the bath and washed with distilled water until the wash-water became colourless; this, even with graphite, China clay, and charcoal, resulted after a few washings, the dye thus being retained by the material in such a manner

that it does not "bleed" into water. It is therefore now definitely established that charcoal, graphite, etc., absorb Night-blue just as do textile fibres, the colouring matter not being washed out by subsequent treatment with water.

The analogy between the absorption of colouring matters by fibrous materials and charcoal, etc., can be further extended by examining the behaviour of the dyed materials towards a neutral soap solution; the dyed cotton, wool, silk, graphite, China clay and charcoal "bleed" freely in hot Marseille soap solution. It seemed desirable to extend the work to the study of the absorption of acid colouring matters towards the same materials. As typical representatives of the three groups of acid colouring matters were selected the nitro-compound Naphthol-yellow S, the azo-colouring matter Ponceau RR, and the sulphonated basic dye Acid-magenta.

TABLE IV.
GRAMS OF DYE ABSORBED.

	Dye used, grams.	Without Acid.			With 4 per cent. H_2SO_4		
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0·08	0·0	0·0	0·0	0·005	0·005	0·005
	—	—	—	—	(0·0625)	(0·0625)	(0·0625)
China clay ...	0·08	0·0	0·0	0·0	0·0024	0·0035	0·0024
	—	—	—	—	(0·03)	(0·0438)	(0·03)
Graphite ...	0·08	0·018	0·0067	0·018	0·017	0·013	0·018
	—	(0·0225)	(0·0084)	(0·0225)	(0·2125)	(0·1625)	(0·225)
Wool	0·6	0·063	0·013	0·063	0·5956	0·566	0·5956
	—	(0·105)	(0·0217)	(0·105)	(0·9927)	(0·9433)	(0·9927)
Charcoal ...	5·5	4·35	3·0	4·35	5·437	5·363	5·402
	—	(0·7909)	(0·5455)	(0·7909)	(0·9886)	(0·9751)	(0·9822)

In this table the amounts of Naphthol-yellow S absorbed by 10 grams of (dry) material, dyed both with and without the addition of sulphuric acid to the dye-bath, are given. It is to be noticed that, without acid, cotton and China clay do not absorb Naphthol-yellow S, and that graphite also absorbs little. Wool and charcoal both absorb very strongly. After dyeing the materials were washed with water; the small quantity of colouring matter absorbed by the graphite is very readily and completely removed by a few washings with distilled water. Dyeing of the cotton, graphite, etc., in the proper sense of the word, therefore does not take place.

Table V. refers to dyeing with Ponceau RR, with and without the addition of acid to the dye-bath.

(a) Without the addition of acid :—Cotton absorbs no Ponceau either in the cold or hot. Graphite absorbs a small amount in the cold, which, however, is expelled on heating and is re-absorbed on cooling. Washing removes the colouring matter absorbed by the graphite quickly and completely. Wool and silk absorb less colouring matter in the hot than in the cold, whilst charcoal absorbs more

in the hot. In every instance the maximum amount of colouring matter is absorbed after cooling.

(b) With the addition of acid :—Cotton and graphite do not absorb colouring matter, either hot or cold. Wool, silk, and charcoal behave

TABLE V.

| | Dye used, grams. | GRAMS OF PONCEAU RR ABSORBED. | | | | | |
| | | Without Acid. | | | With 4 por cent. H₂SO₄. | | |
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0·2	0·0	0·0	0·0	0·0	0·0	0·0
Graphite ...	0·2	0·0462	0·0	0·0463	0·0	0·0	0·0
	—	(0·231)	(0·0)	(0·2315)	—	—	—
Wool	1·0	0·0889	0·064	0·12	0·387	0·807	1·0
	—	(0·0889)	(0·064)	(0·12)	(0·387)	(0·807)	(1·0)
Silk	1·0	0·19	0·096	0·192	0·264	0·576	0·713
	—	(0·19)	(0·096)	(0·192)	(0·264)	(0·576	(0·713)
Charcoal ...	5·5	5·31	5·438	5·5	5·428	5·473	5·5
	—	(0·9655)	(0·9887)	(1·0)	(0·9869)	(0·9951)	(1·0)

analogously in that they absorb more dye in the hot than in the cold, and take up a further quantity on cooling. On washing with water it is distinctly noticeable that the materials dyed with the addition of acid are more quickly freed from the loosely-held colouring matter than those dyed without the acid.

It was deemed of interest to ascertain whether charcoal containing the same proportion of colouring matter as the wool would hold it in a similar manner. For this purpose 10 grams of (dry) charcoal were allowed to absorb 1 gram of Ponceau RR, with and without the addition of acid, respectively. Charcoal treated in this manner does not allow any of the colouring matter to "bleed," either into cold or hot water, and none can be extracted if soda is added to the wash-water; the colouring matter is therefore more firmly held by the charcoal than by the wool.

TABLE VI.

GRAMS OF ACID-MAGENTA ABSORBED.

| | Dye used, grams. | Without Acid. | | | With 4 per cent. H₂SO₄. | | |
		Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton	0·1	0·0	0·0	0·0	0·0	0·0	0·0
Graphite ...	0·1	0·0	0·0	0·0	0·0	0·0	0·0
Wool	0·5	0·0334	0·0212	0·0518	0·386	0·467	0·5
	—	(0·0668)	(0·0424)	(0·1036)	(0·772)	(0·934)	(1·0)
Silk	0·5	0·222	0·067	0·233	0·469	0·371	0·477
	—	(0·444)	(0·134)	(0·466)	(0·938)	(0·742)	(6·954)
Charcoal ...	3·25	2·905	2·5	2·784	3·2387	2·803	3·2394
	—	(0·8938)	(0·7692)	(0·8566)	(0·9965)	(0·8625)	(0·9967)
Lamp black ...	1·0	0·317	0·058	0·244	0·5296	0·1874	0·3649
	—	(0·317)	(0·058)	(0·244)	(0·5296)	(0·1874)	(0·3649)

Experiments carried out with Acid-magenta show that no colouring matter is absorbed by cotton or graphite if dyed either with or with-

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out the addition of acid to the dye-bath. Wool, silk and charcoal, dyed without the addition of acid, absorb less colouring matter in the hot than in the cold, but take up more on cooling. Silk and charcoal, dyed with the addition of acid, exhibit parallel behaviour

TABLE VII.

GRAMS OF DIAMINE SKY-BLUE FF. ABSORBED.

	No addition.			With 15 grams Na₂SO₄.			With 0·6 gram Na₂CO₃.		
	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton …	0·0442 (0·1105)	0·0075 (0·0188)	0·0578 (0·1445)	0·3171 (0·7927)	0·2269 (0·5672)	0·3654 (0·9135)	0·0712 (0·178)	0·0471 (0·1178)	0·121 (0·3025)
Artificial silk	0·0308 (0·077)	0·016 (0·04)	0·08 (0·2)	0·3059 (0·7647)	0·32 (0·8)	0·4 (1·0)	0·0572 (0·143)	0·0308 (0·077)	0·1091 (0·2728)
Graphite …	0·3714 (0·9285)	0·1757 (0·4393)	0·3035 (0·7587)	0·1932 (0·483)	0·2378 (0·5945)	0·1333 (0·333)	0·0757 (0·1892)	0·08 (0·2)	0·0757 (0·1893)
China clay …	0·0571 (0·1428)	0·0735 (0·1837)	0·0429 (0·1073)	0·0471 (0·1178)	0·1 (0·25)	0·0364 (0·091)	0·0308 (0·077)	0·1126 (0·2815)	0·016 (0·04)
Wool …	0·0	0·0	trace	0·0096 (0·024)	0·1042 (0·2605)	0·188 (0·47)	0·0	0·0	0·0
Silk …	0·2323 (0·5807)	0·3117 (0·7792)	0·3826 (0·9565)	0·3529 (0·8823)	0·3633 (0·9083)	0·4 (1·0)	0·0	0·0	—
Charcoal …	1·743 (0·581)	2·9659 (0·9886)	3·0 (1·0)	1·816 (0·6053)	2·8286 (0·9429)	2·9386 (0·9795)	1·7 (0·5666)	2·95 (0·9833)	3·0 (1·0)

GRAMS OF CONGO-RUBINE ABSORBED.

	No addition.			With 15 grams Na₂SO₄.			With 0·6 gram Na₂CO₃.		
	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.	Cold.	Hot.	Cooled.
Cotton …	0·1273 (0·3183)	0·0889 (0·2222)	0·1447 (0·3617)	0·2942 (0·7355)	0·2208 (0·552)	0·3045 (0·7612)	0·1778 (0·4445)	0·1436 (0·359)	0·1895 (0·4737)
Graphite …	0·3527 (0·8817)	0·2889 (0·7222)	0·3487 (0·8718)	0·3385 (0·8462)	0·2095 (0·5238)	0·3375 (0·8438)	0·1561 (0·3903)	0·1576 (0·394)	0·156 (0·39)
Wool …	0·1059 (0·2647)	0·1531 (0·3827)	0·1949 (0·4872)	0·2333 (0·5833)	0·2676 (0·669)	0·3692 (0·923)	0·1059 (0·2648)	0·1241 (0·3104)	0·15 (0·375)
Charcoal …	2·1304 (9·7101)	2·975 (0·9917)	3·0 (1·0)	2·3846 (0·7949)	2·9385 (0·9795)	2·961 (0·987)	2·3939 (0·798)	2·92 (0·9733)	3·0 (1·0)

Material, 10 grams (charcoal, 5 grams). Dye bath (750 c.c.) containing 0·4 gram (in the case of charcoal, 3·0 grams) of dye.

in that they absorb less colouring matter in the hot than in the cold, but take up slightly more on cooling. Wool, under these conditions, absorbs more dye hot than cold, and still more on cooling.

On washing the Acid-magenta dyeings it was in every instance noticed that more colouring matter is removed than in the case of Ponceau RR, the dyeings with the addition of acid being invariably faster than those without acid. The colouring matter is more readily washed out from the silk than from charcoal or wool. It is thus shown that the analogy pointed out between the absorption of basic dyes by fibrous and inert absorbents extends with remarkable precision to the absorption of acid colouring matters. It was still necessary to ascertain whether the analogy also extends to the behaviour of the absorbents towards the colouring matters which dye cotton direct; as one of these Diamine Sky-blue FF was selected. The results are given in Table VII.

The following classification of the results facilitates their comparison :—

(a) Material dyed without any addition to the dye-bath :—Cotton and graphite both "bleed" distinctly with cold water, cotton rather more freely than graphite. Both "bleed" more freely in hot water and still more colouring matter is removed when sodium carbonate or soap is added to the water. Silk "bleeds" hardly appreciably in the hot, a little more when sodium carbonate is added, and still more with soap.

(b) Material dyed with the addition of sodium sulphate :—Cotton "bleeds" less than in (a), either hot or cold; soda and soap remove the dye more freely. Graphite does not "bleed" appreciably, either hot or cold, and very little with sodium carbonate or soap. It is quite evident that the graphite holds the dye more strongly than does the cotton. The silk "bleeds" comparatively less than in (a), especially when it is considered that a much greater proportion of colouring matter has been absorbed.

Artificial silk, if compared with cotton, "bleeds" distinctly less, either with or without the addition of sodium sulphate. The dyed wool scarcely "bleeds" in hot water, but the addition of soap or sodium carbonate removes the colouring matter very freely. Charcoal, dyed both with or without the addition of sodium sulphate, resists the action of hot or cold water very well. Sodium carbonate does not remove the dye to any appreciable extent, but with soap and sodium carbonate the colour "runs" very freely. It therefore behaves very similarly to wool.

With the exception of a few dyes, such as the Diamine Sky-blue FF, used above, the colouring matters dyeing cotton direct show a great affinity for the wool fibre; it was therefore of importance to study a dye of this class which dyes wool readily, and for this purpose Congo-rubine was selected. The results obtained are also given in Table VII. It is seen that when dyed with Congo-rubine, without any other addition to the dye-bath, cotton behaves similarly to graphite, whilst wool is dyed like charcoal. When dyed with the addition of sodium sulphate, cotton, as before, behaves analogously

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to graphite, and wool to charcoal. Both the dyed cotton and graphite "bleed" very little with cold water, more distinctly with hot water, and still more freely with the addition of sodium carbonate or soap. The dyed wool and charcoal also behave very similarly in that they "bleed" but little with hot water and more freely with sodium carbonate or soap. The dyed charcoal and wool both bleed comparatively less when dyed with the addition of sodium sulphate. It seemed desirable to make a series of experiments on the absorption of substances other than coal-tar dyes by these materials. The following experiments were undertaken with a view to ascertain whether iodine and colouring matters are absorbed in a similar manner by wool. Ten grams of (dry) wool were immersed in 750 cc. of potassium iodide solution containing 1·905 grams of free iodine. The time of immersion varied as shown in Table VIII.

TABLE VIII.

Time of immersion in hours...	1.	6.	18.	72.
grams absorbed...	1·32	1·62	1·767	1·848
	(0·6929)	(0·8504)	(0·9276)	(0·9701)

Inspection of the table shows that the absorption of iodine by wool proceeds similarly to the absorption of Night-blue.

A comparison was next made of the mode in which iodine was absorbed by textile fibres and by inert absorbents (Table IX.).

TABLE IX.

10 grams (dry) of material immersed 72 hours in 750 cc. of potassium iodide solution containing 7·62 grams of free iodine.

	Grams absorbed.			Grams absorbed.
Cotton ...	0·136 (0·0178)	Wool	4·4	(0·5774)
Graphite ...	0·9 (0·1181)	Charcoal ...	7·35	(0·9646)
China clay ...	0·56 (0·0735)			

The table shows that cotton and China clay absorb a small amount of iodine, whilst graphite absorbs rather more; wool and charcoal absorb very large quantities. Washing with water alone, removes the iodine very quickly and completely from cotton, China clay and graphite. Wool and charcoal retain the iodine much more firmly, a large amount of iodine remaining on both materials after washing with water. The colour of the wool containing iodine is a deep brown orange, and the iodine can be removed completely from both wool and charcoal by solvents such as alcohol or potassium iodide.

It is remarkable that iodine behaves towards all these absorbents similarly to acid dyes.

The foregoing absorption experiments prove conclusively that dyeing with basic colouring matters, with the three different types of acid dyes and with the colouring matters dyeing cotton direct, proceeds in a closely analogous manner independently of whether textile fibres or inert substances, such as charcoal, graphite, etc.,

are employed as absorbents. It may therefore be safely concluded that all these dyeing processes are due to purely physical or mechanical absorption. The correctness of this view is strongly supported by the results obtained on comparing the action of hot and cold water, of sodium carbonate, soap, etc., on the dyed materials, both fibres and inorganic absorbents exhibiting a remarkable degree of analogy of behaviour towards these treatments.

NOTE ON ERIKA PINK. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1901, No. 6. It is well known that ordinary Erika B dyed on cotton yields a pink which, in common with the other direct cotton colours, shows the undesirable property of "bleeding" on washing. With a view to remedying this defect, the author produced the insoluble (unsulphonated) dyestuff on cotton in the following way. Dehydrothiometaxylidine was dis- solved in spirit and the solution stirred into water. In this milky suspension cotton was dyed, first in the cold and ultimately at the boil for an hour. The colour was then produced on the fibre by diazotising and developing in beta-naphthol in the usual manner. For brilliancy the colour does not equal ordinary Erika, though it is brighter than Turkey pink. Though fast to washing, and even to ordinary bleaching, the colour was found to be extremely loose to light.

ON THE BEHAVIOUR OF THE BASIC DYES TOWARDS WOOL AND SILK. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1902, No. 4. The paper relates in the main to Witt's solution theory of dyeing. The author shows that if silk dyed with night blue is extracted with alcohol, and the alcoholic solution (after evaporating to a small bulk) be run into a-dilute warm solution of barium hydrate, the whole of the bright blue is separated in the form of its insoluble base. If the filtered solution is treated with carbon dioxide to remove the barium, then filtered again and evaporated to dryness, it leaves a yellow amorphous substance which, dissolved again in water, was found to precipitate not only night blue, but other basic dyes. Wool dyed with night blue behaved similarly.

NOTE ON THE THEORY OF DYEING. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1900, No. 6. In this paper, which is controversial in character, the author refers to an experiment described by M. P. Sisley in which amyl alcohol is said to be coloured red by shaking with a colourless solution of rosaniline. It is now shown that if the amyl alcohol is previously purified by shaking with caustic soda and distilling, and if the carbonic acid of the air be excluded when performing the experiment, no red colouration occurs.

TITANIUM SESQUIOXIDE AND ITS SALTS AS REDUCING AGENTS. EDMUND KNECHT. "Ber. d. Deutschen Chem. Ges." 1903, page 166. The author describes the preparation of titanous chloride, and draws attention to its powerful reducing properties. Thus, by adding titanous chloride to a solution of sulphurous acid, free hydrosulphurous acid is formed in considerable amount. Nitro compounds are at once reduced to the corresponding amines, while azo dyes are decolourised in a few seconds. Indigo is rapidly reduced to indigo white, whereas on warming with excess of the reagent it is over-reduced, passing into a yellow crystalline body. Prussian blue is almost instantly decolourised, the colour returning on exposure to the air. Unsaturated compounds may be reduced to saturated compounds by prolonged heating with the reagent. Thus fumaric acid was reduced to succinic acid and citraconic acid to pyrotartaric acid.

TITANOUS CHLORIDE IN VOLUMETRIC ANALYSIS.—I. EDMUND KNECHT and EVA HIBBERT. "Ber. d. Deutschen Chem. Ges." 1903, page 1549. In the first part of the paper the authors show that the reduction of ferric salts by titanous chloride takes place quantitatively according to the equation

$$TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2,$$
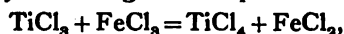
and that this reaction can be employed either for the estimation of iron (see this "Journal," Part 2, page 243) or of titanium. The titration of azodyes and nitro compounds is also described.

TITANOUS CHLORIDE IN VOLUMETRIC ANALYSIS.—II. EDMUND KNECHT and EVA HIBBERT. "Ber. d. Deutschen Chem. Ges." 1905, page 3318. The first part of the paper deals with the volumetric estimation of indigo and other dyestuffs which yield colourless leuco compounds (see this "Journal," No. 2, page 253).

Hydrogen Peroxide. If a dilute solution of titanous chloride be added to a solution of hydrogen peroxide, the well-known intense orange yellow colouration of TiO_3 is at once produced. By continuing to add the titanous chloride slowly the colour increases in intensity up to a certain point, then gradually fades and ultimately vanishes altogether. The reaction is complete when the equation

$$2\ TiCl_3 + H_2O_2 + 2\ HCl = 2\ H_2O + 2\ TiCl_4$$

is fulfilled, so that $H_2O_2 = 2\ TiCl_3 = 2$ Fe. To carry out the titration 10 cc. of the technical hydrogen peroxide solution are made up to 250 cc., and of this 10 cc. are titrated with standardised titanous chloride until the colour disappears. From the number of cubic centimetres used for titrating, the amount of hydrogen peroxide is ascertained and may be expressed either as such or in volumes of oxygen. The process was found to give the same results as the iodimetric and permanganate processes.

Ammonium persulphate is estimated by adding to the solution of a known weight a known amount (excess) of titanous chloride solution. The excess of the latter is titrated back with standard iron alum. The calculation is based on the oxidising power of the persulphate, $NH_4SO_4 = Fe$. The process gave the same results as the iodimetric process.

Tin. The finely-divided metal is dissolved in hydrochloric acid in a 100 cc. flask provided with a Bunsen valve. To accelerate solution the contents of the flask may be gently heated on a water bath, but must on no account be boiled, as this was shown to cause considerable loss due to the volatility of stannous chloride in presence of hydrochloric acid. When the tin is dissolved, the contents of the flask are cooled and made up to 100 cc. 25 cc. of the solution are then withdrawn and run straight into excess of iron alum solution contained in a flask through which a current of CO_2 is maintained. After warming for some minutes, the contents of the flask are cooled and the excess of iron alum titrated as usual with titanous chloride. $Sn = 2\ TiCl_3 = 2\ Fe$. The process is also applicable to the analysis of stannous chloride.

TITANOUS CHLORIDE IN VOLUMETRIC ANALYSIS.—III.

EDMUND KNECHT and EVA HIBBERT. "Ber. d. Deutschen Chem. Ges." 1907, page 3891. Although the estimation of picric acid by the indirect process (see this "Journal," No. 2, page 251) at once gave good results, its homologues, trinitrocressol and trinitroxylenol, were found on a previous occasion to show only 90% of the theoretical oxidising power. In the reduction of picric acid, the NO_2 groups which occupy the ortho position to the OH group are first reduced, that occupying the para position offering greater resistance to reducing agents. Nevertheless, the reduction can be completed by using a comparatively slight excess of titanous chloride. It was now found that by using a large excess of the reducing agent and boiling for about five minutes, the two homologues could be titrated with accuracy. It is surmised that the difficulty experienced in reducing these two nitro compounds is due to steric hindrance caused by the presence of the CH_3 group in meta position to the OH group.

The authors further describe the titration of nitro compounds that are insoluble in water and are difficult to sulphonate, such as dinitrobenzine, dinitrotoluene and dinitronaphthalene.

For the majority of the direct cotton colours an improved method is described. Formerly these were done by the indirect method—adding excess of titanous chloride and titrating back with iron alum. By the addition of Rochelle salt to the aqueous solution of the dyestuff the authors now find that the titration can be effected directly, and the process is thus considerably simplified.

The titration of the inner anhydride of $p.p^1$ tetramethyldiamidodi-

phenyl *m* tolylcarbinol *o* sulphonic acid, a dyestuff discovered by T. Sandmeyer,* is described. The end point of the reaction is extremely sharp, and the result approximates very closely to the theoretical. The reason why this particular dyestuff is specially alluded to is that it is the only dyestuff which the authors have found to precipitate tannic acid and not gallic acid from an aqueous solution of a tannin in presence of sodium acetate. The hope is expressed that these conditions may form the basis of a satisfactory method of estimating tannic acid.

Iron. Originally, the authors recommended a spot reaction with potassium sulphocyanide in determining the end point of the reaction between ferric salts and titanous chloride. This method has now been entirely abandoned by them, the sulphocyanide being added directly, and in considerable excess, to the contents of the flask. For the estimation of ferrous and ferric iron in solution, the following *modus operandi* is recommended. The ferric iron is first titrated directly by titanous chloride in an aliquot porton of the solution. To another portion of the solution ammonia is added and then hydrogen peroxide. The solution is then boiled for two minutes to destroy the excess of hydrogen peroxide, acidulated with hydrochloric acid, and titrated again. This gives the total iron, and the amount of ferrous iron is calculated from the difference between total iron and ferric iron.

Hydrosulphite of Soda. The process worked out by the authors is intended for the valuation of the solid hydrosulphite, which now comes into the market in very large quantities. The difficulties encountered in the titration of this product by any of the older processes (*e.g.* with indigo carmine) are twofold. In the first place, it at once begins to decompose when dissolved in water, so that no reliable results could be obtained from such a solution. The decomposition can be prevented by dissolving in dilute caustic soda, but one is met here at once with a still more serious difficulty, inasmuch as the alkaline solution immediately begins to absorb oxygen from the air at such a rate that a few seconds exposure will suffice to vitiate the ultimate result. The authors have succeeded in overcoming these difficulties in the following way. A known weight of the hydrosulphite (o·2 grm.) is added directly to a known volume containing a larger amount of standardised methylene blue solution than the hydrosulphite is capable of reducing. The methylene blue solution is contained in a conical flask through which a current of CO_2 is maintained. The hydrosulphite in dissolving, instantly reduces its equivalent of methylene blue, and the excess of the latter is estimated, after acidulating the solution with acetic acid, by titration with standardised titanous chloride solution. The calculation of the result is simple, inasmuch as 2 Fe represent one molecule of $Na_2S_2O_4$.

In place of Methylene blue indigo carmine solution may be used, and the titanous chloride may be replaced by hydrosulphite of soda standardised either on copper sulphate or indigotine.

SOME FURTHER OBSERVATIONS ON THE ACTION OF NITRIC ACID ON CELLULOSE. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," March, 1904, No. 3, vol. 20.

In a previous paper ("Journal of the Society of Dyers & Colourists," 1896, page 89) entitled "Note on the Action of Nitric Acid on Cotton," the results of some experiments which I had carried out on the action of nitric acid of different strengths on calico and on cotton yarn were communicated. The results showed that up to 62°Tw. there was scarcely any perceptible action, but at 82°Tw. the action of the acid resembled that of strong caustic soda, inasmuch as it had the effect of mercerising the cotton. Since that time the mercerising action of nitric acid has become fairly generally known, and has been the subject of several patents, such as those of Scheulen, in which textile fibres generally are subjected to the action of strong nitric acid under tension with the object of producing a permanent gloss. That such an effect could be obtained on cotton yarn in this manner I recognised in 1896, some months after the reading of my paper, but on account of the expense and the danger attending the use of nitric acid on a large scale, I did not foresee any practical application of the process.

Some three years ago I again took up the study of the action of nitric acid on cotton with a view to ascertaining, if possible, whether any definite chemical changes could be traced in its action on cellulose, similar to those given by Mercer to account for the changes which take place in the cotton fibre when it is acted upon by strong caustic soda. As is well known, these changes are represented as taking place in such a manner that the cellulose first combines with the caustic soda to form a definite compound $(C_6H_{10}O_5)_2 \cdot Na_2O$, which is decomposed on washing with water into caustic soda and a hydrated cellulose. When cotton is steeped in nitric acid of 83° Tw. it very soon acquires a gelatinous appearance, in fact, to judge from appearances, the action would appear to have reached a maximum in the course of two minutes. Taken out of the acid and washed with water till neutral, the material resumes its normal appearance, but is found to have shrunk considerably, at the same time acquiring increased strength, an increased amount of moisture in the air-dried condition, and a greater affinity for direct colours; in fact, it shows properties similar to cotton mercerised with caustic potash, which are known to be not so pronounced as those shown by cotton mercerised with caustic soda of the same strength. Its affinity for direct and sulphide colours is, however, greater than that of ordinary mercerised cotton.

Attempts were made to remove the excess of acid from cotton so treated by means of solvents, but without success. It was sub-

sequently found, however, that after having removed as much acid as possible by pressing between filter paper, the rest of the uncombined acid could be got rid of by leaving the material in a vacuum over freshly-burnt lime for three to four days. When taken out it is crisp to the feel, fumes strongly in moist air, and if pressed tightly between finger and thumb gives one the impression of being hot. In this condition the material appears to represent a combination of cellulose with nitric acid corresponding nearly to the formula, $C_6H_{10}O_5 \cdot HNO_3$. The compound is instantly decomposed by water into free nitric acid and a slightly nitrated cellulose, which is, however, considerably tendered. The estimation of the nitric acid was effected by steeping a known weight of bleached and purified cotton yarn in nitric acid of 83° Tw., drying over lime in a vacuum desiccator, and after transferring the dried compound to a beaker containing distilled water, titrating directly with normal sodium carbonate and methyl orange as indicator. The amount of nitric acid thus found experimentally was 35·8 per cent., while, according to theory, 37·2 per cent. should have been present. The low figure is probably due to the fact that the compound gradually loses nitric acid in the desiccator, and it is impossible to exactly hit the point at which the mechanically-adhering acid is evaporated. In its behaviour towards nitric acid, cellulose would appear to be analogous to phenanthrene quinone, which, according to Kehrmann, yields with ordinary strong nitric acid a definite nitrate forming beautiful orange-red crystals, which are instantly decomposed by water into phenanthrene quinone and nitric acid. These crystals also lose their nitric acid in a vacuum over lime, but much more rapidly than is the case with the cellulose compound. Both are stable, however, when kept in close vessels.

According to Cross and Bevan the cellulose molecule probably contains a ketonic group, and, assuming this for the moment to be correct, we might represent the formation of the unstable nitrate by analogy with Kehrmann's results as follows :—

$$CH_2(CH_2OH)_4CO + HNO_3$$
$$= CH_2(CH_2OH)_4C \diagup^{ONO_2}_{OH.}$$
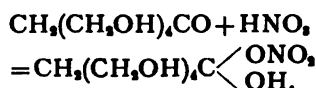
It is not probable that the nitric acid should attack the hydroxyl groups which are known to exist in the cellulose molecule, as a stable nitrate would thereby result. Though stable at the ordinary temperature when kept in a closed vessel, the new nitrate is rapidly decomposed if heated to 100°, with copious evolution of nitrous fumes. When the action has ceased a residue is left consisting of a friable white substance completely soluble in cold caustic soda, and to a great extent soluble in ammonia. The solution in caustic soda gives a copious precipitate with Fehling's solution. From its behaviour the product would appear to be identical with the oxy-

cellulose obtained by Cross and Bevan by boiling cotton with a large excess of 60 per cent. nitric acid.

In my previous communication I drew attention to the remarkable fact that cotton mercerised with nitric acid exhibits an affinity for certain acid colours. In titrating the nitrate with methyl orange as indicator we were struck by the fact that when the reaction was over the colour could not be removed from the cotton by washing, and we were thus induced to try the behaviour of this material towards various dyestuffs, comparing it with ordinary cotton and with cotton mercerised by a short immersion in strong nitric acid. The result of a series of comparative dye-trials showed that the cotton which had been dried with the acid in it had acquired an affinity for certain acid dyes (crystal scarlet, acid violet, etc.) almost equal to that of an animal fibre, but in the same degree as it gained an affinity for these dyestuffs it lost its affinity for the direct colours. At the same time, however, the three samples did not show any material difference in their behaviour towards methylene blue. As was pointed out at the beginning of the paper, nitric acid of 62° Tw. was found on a former occasion to be practically without action on cellulose. With the object of ascertaining at what degree of concentration the formation of the nitrate and consequent nitration takes place, a series of experiments was carried out with acids of various strengths, the results of which are shown in the table :—

Strength of Acid.	Amount absorbed by fibre.	Contraction.
20° Tw.	2·0%	1%
40° „	3·7%	1%
60° „	3·8%	1%
65° „	7·1%	1%
70° „	7·4%	1%
75° „	7·5%	1%
76° „	11·7%	2½%
80° „	27·3%	10%
83° „	35·8%	13%

From this it would appear that the action of the acid takes place in three phases, of which the third (at which mercerisation begins) takes place quite suddenly, viz., at 76° Tw. If the concentration of the acid is taken beyond 83° Tw. the amount of nitric acid taken up increases somewhat, but at the same time the degree of actual nitration rapidly increases. Thus cotton steeped in nitric acid of 90° Tw. was found to contain 40·6 per cent. after drying, but was found after drying to be nitrated to such an extent that it showed in places a decreased affinity for Erika as compared with ordinary cotton. Cotton steeped for two minutes in acid of 1·415, and then washed, was found to contain only 0·54 per cent. of combined nitrogen. When steeped in the acid for a longer period the amount

of nitric acid firmly combined with the cellulose increases, but at the same time there is a decrease in the strength of the material.

In conclusion I may say that what I claim to have established is that when cellulose in the form of bleached cotton is treated with nitric acid of 1·415 sp. gr. (i.e., the acid which shows a constant boiling point of 120° ·5) combination of the acid with the fibre ensues so as to form a nitrate which corresponds very nearly to the formula, $C_6H_{10}O_5 \cdot HNO_3$, and which is resolved by water into a hydrated cellulose and nitric acid. Cotton steeped in concentrated hydrochloric acid, in glacial acetic acid, and in anhydrous formic acid, was found to retain, after squeezing and drying over lime in a vacuum, only very small quantities (two to three per cent.) of these acids.

My best thanks are due to Mr. G. T. Yates and to Miss E. Hibbert for their assistance in the above investigation.

ON THE THEORY OF DYEING. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1904, No. 3. Many years before the publication of my first communications on the theory of dyeing, it was argued by the adherents of the mechanical theory that there was no evidence of chemical action taking place during the dyeing process, such as alteration in temperature, a more or less complete change in the properties of the re-acting substances, and above all, the absence of any regularity in their relative quantities. Writing on this subject as far back as 1860, Chas. O'Neill[1] points out that Walter Crum's objection that if there were chemical combination there should be disorganisation of the fibrous structure, is ruled out of order by choosing guncotton as an example. This substance, though deeply and permanently altered in its chemical properties, would pass in the hands of most persons as ordinary cotton. O'Neill further remarks that in dyeing only a very small portion of the fibre can be in actual chemical combination. In 1889[2] I endeavoured to show, however, that in the dyeing of wool, the laws which govern chemical combination are in some cases obeyed. My experiments were done at the time with three acid dyes—Picric acid, Naphthol Yellow S, and Tartrazine—and with one basic dye—Crystal Violet. With regard to the behaviour of the basic dyes, I hope to be able to make a further communication at a later date, but with regard to the acid dyes—Picric acid and Naphthol Yellow (I will except Tartrazine because subsequent investigations have shown that its then accepted formula was incorrect)—I showed by means of quantitative determinations that when wool is dyed with a large excess of either of these dyestuffs, they are taken up about in the proportion of their molecular weights.

Further work in this direction was not possible at the time, because no processes were available by means of which other dyestuffs

(1) "Chemistry of Calico Printing, Bleaching, and Dyeing."
(2) "Journal of the Society of Dyers and Colourists," 1889, page 74.

could be estimated with a sufficient degree of accuracy (the colori-
meter not being exact enough for such estimations). But since I
have succeeded in working out an absolute method[3] by means of
which the azo dyes can be estimated with great accuracy, I saw the
possibility of attacking the question more profoundly. As the result
of my investigations, I am able to show that in homologous series
the amounts of the acid dyes taken up by wool are in proportion to
their molecular weights. In the new experiments which I am about
to detail only such colouring matters were compared with each
other as belong to homologous or analogous series. It was neces-
sary to prepare these first in the chemically pure condition in order
in the first instance to obtain strictly comparable figures, and
secondly to obviate the disturbing influence of Glauber salt, or
common salt, usually contained as accidental impurities or as
diluents in the commercial articles. For it is well known from the
researches of Hallitt[4] that the presence of these salts in the dyebath
exercises a restraining influence on the amount of colour taken up
by the fibre. All the dyestuffs used (with the exception of cresso and
xylo-picric acids) yielded after drying at 140-150°C., on titrating
with $TiCl_3$ figures which showed them to be chemically pure. I was
disappointed to find that cresso-picric and xylo-picric acids differed
materially from ordinary picric acid in their behaviour towards
titanous chloride, and could not be estimated by that means. But
having convinced myself of the purity of my products by other
means, I found that they could be accurately estimated by the old
Night Blue process of Rawson.[5]

The dyeing of the wool was conducted as in my previous experiments
with a large excess (50, 25%, etc.) of colouring matter at the boil,
and with the addition of 30 per cent. sulphuric acid, for one hour.

This apparently excessive quantity of acid was employed on account
of the extraordinarily high percentages of dyestuff used. The dyeing
was done in open vessels, the amount of water in the dyebath being
about 100 times the weight of the wool. As evaporation took place
the water in the dyebaths was replenished. It might appear at first
sight that this mode of procedure would not be sufficiently exact to
obtain accurate results, and I should not have ventured to use it
had I not satisfied myself that the amount of water used had, within
fairly wide limits (50-200 times the weight of the wool) no material
influence on the amount of dyestuff taken up by the fibre. From
other blank experiments it was ascertained that wool boiled for an
hour in water with the addition of 30 per cent. sulphuric acid yielded
nothing to the bath which might interfere with the accuracy of the
results. As in my previous experiments, the amounts of colour
taken up by the fibre were estimated indirectly, by titrating the dye-
stuff remaining in the bath (or in some cases an aliquot volume of

(3) " Journal of the Society of Dyers and Colourists," 1903, page 159.
(4) " Journal of the Society of Dyers and Colourists," 1899, page 31.
(5) " Journal of the Society of Dyers and Colourists." 1888, page 82.

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the bath), with titanous chloride. The difference between the figures obtained in this manner and the amounts of dyestuff originally employed gave the amounts taken up by the fibre. A re-examination of my former results with picric acid and naphthol yellow S by means of the more exact method with titanous chloride yielded figures which differ slightly from those obtained at that time.

	Found.	Calc.
Picric acid	12˙58	—
Naphthol Yellow S.....	20˙80	21˙38%

The naphthol yellow S employed for this purpose was the chemically pure di-potassium salt,[6] which was found to give accurate results by the titanous chloride method. The new experiments were conducted with five series of colouring matters, viz. :—

First series. Orange G (sodium salt of the dyestuff from diazotised aniline and G salt), mol. wght.—452; and crystal scarlet (sodium salt of the dyestuff from diazotised alphanaphthylamine and G salt), mol. wght.—502.

Dyestuff.	Amount used.	Amount taken up by fibre.	Calculated.
Orange G...	50%	16˙24%	—
Crystal Scarlet	50%	18˙23%	18˙02%
Orange G...	25%	15˙68%	—
Crystal Scarlet	25%	17˙42%	17˙40%

The calculated amounts of crystal scarlet are obtained from the amounts of Orange G obtained under similar conditions by multiplying by the fraction $\frac{502}{452}$. In the subsequent series the calculated amounts are obtained by a similar mode of procedure.

Second series. Scarlet 2G (sodium salt of the dyestuff from diazotised aniline and R salt), mol. wght.—452; and xylidine scarlet (sodium salt of the dyestuff from diazotised metaxylidine and R salt), mol. wght.—479.

Dyestuff.	Amount used.	Amount taken up by fibre.	Calculated.
Scarlet 2G	50%	16˙37%	—
Xylidine Scarlet	50%	17˙12%	17˙30%
Scarlet 2G	25%	15˙53%	—
Xylidine Scarlet	25%	16˙22%	16˙40%

Third series. Orange II (sodium salt of the dyestuff from diazotised sulphanilic acid and beta-naphthol), mol. wght.—350; and Fast Red A (sodium salt of the dyestuff from diazotised naphthionic acid and beta-naphthol), mol. wght.—400.

(6) " Berl Ber.", page 3475, 1904.

Dyestuff.			Amount used.	Amount taken up by fibre.	Calculated.
Orange II.	...	...	...	50%	20·40%	—
Fast Red A	...	...	...	50%	23·38%	23·30%
Orange II.	...	...	...	25%	16·46%	—
Fast Red A	...	...	...	25%	18·75%	18·80%

Fourth series. Fast Acid Magenta B (sodium salt of the dyestuff from diazotised aniline, combined in alkaline solution with H acid), mol. wght.—489, and the sodium salt of the dyestuff obtained by combining diazotised alpha-naphthylamine with H acid in alkaline solution, mol. wght.—539.

Dyestuff.	Amount used.	Amount taken up by fibre.	Calculated.
Fast Acid Magenta B ...	50%	16·71%	—
Corresp. Naphthylamine			
Compound	50%	18·66%	18·41%

Fifth series. Picric acid, mol. wght.—229. Cresso-picric acid (sym. trinitrocressol), mol. wght.—243, and Xylo-picric acid (sym. trinitroxylenol), mol. wght.—257.

Dyestuff.	Amount used.	Amount taken up by fibre.	Calculated for Picric Acid = 12·58%	Calculated for Trinitrocressol — 14·60%
Picric acid... ...	50%	12·58%	—	—
Trinitrocressol ...	50%	14·60%	13·40	—
Trinitroxylenol ...	50%	15·28%	14·10	15·40

From the results obtained in this last series it will be seen that Picric acid shows in comparison with its homologues a somewhat abnormal behaviour. But if the amounts of Cresso-picric acid and Xylo-picric acid taken up by wool under similar conditions be compared, it will be seen that they behave like the azodyes in the four preceding series. In dyeing wool with increasing amounts of the dyestuffs mentioned in the various series, it is interesting to note that in each case a limit is reached, beyond which very little more colouring matter is taken up by the fibre. This may be exemplified by the following series, which has been worked out for crystal scarlet :—

Percentage of colour used...   50·0   25·0   22·5   20·0   17·5   15·0

,,   taken up by fibre   18·2   17·3   17·0   16·6   15·3   14·2

Percentage of colour used... 12·5   10·0   7·5   5·0   2·5

,,   taken up by fibre 11·9   9·6   7·2   4·7   2·2

If a curve is constructed in which the percentages of colour used are shown on one co-ordinate, and the percentages taken up by the fibre on the other, it is seen to follow almost a straight line until the

amount of colour absorbed reaches about 17 per cent., when it suddenly turns and follows a course almost parallel to one of the co-ordinates. The results which it has been my privilege to communicate practically speak for themselves, in showing that when wool is dyed with large excesses of a number of acid colours, the latter are taken up not indiscriminately, but in the proportion of their molecular weights. The view which I formerly expressed that chemical processes underlie the dyeing of wool thus receives a strong confirmation. What the nature of these processes is—whether it be a question of salt formation or condensation in the nucleus, or whether the bodies formed belong to a hitherto unknown class of substances—I cannot for the present decide. It is quite possible that the process is different with different classes of colouring matters; in fact, this appears to be probable in the case of the acid and basic colours.

The rôle played by the sulphuric acid in dyeing wool with acid colours is usually explained by the assumption that it merely liberates the free colour acid from its salt (usually the sodium salt in commercial dyestuffs), which is then taken up by the fibre. That the amount of acid usually employed in dyeing, though theoretically sufficient, is quite inadequate to completely liberate the free colour acid has been clearly demonstrated by the beautiful researches of Sisley on the azodyes. It is further evident from the behaviour of the free colour acid of Fast Red A in dyeing. For while this substance is taken up by the fibre in slightly larger amount than its sodium salt, only a thin shade results, and in either case the greater part of this colour remains in the bath. It is therefore in another direction that we must look for an explanation. I have shown in a former paper that when wool is boiled in dilute sulphuric acid and then repeatedly in distilled water until no more acid is given up, it can be dyed with ordinary acid colours without additions to the bath yielding fuller shades than when these colours are dyed in the ordinary way. The same thing I now find applies to wool which has been boiled in benzene sulphonic acid and then repeatedly in distilled water, and this fact would explain the greater affinity of the free colour acid of Fast Red A as compared with its sodium salt. I have further shown on a previous occasion that if the sulphuric acid is taken of sufficient strength to partially disintegrate the wool fibre, the solution is found to contain a substance which precipitates the acid colours, yielding intensely coloured lakes. In this case the decomposition of the fibre had, however, resulted in the formation of soluble proteids (lanuginic acid), and no direct comparison with the dyeing process can consequently be made. That, however, the sulphuric acid employed with the acid dyes acts in a sense in the capacity of a mordant (more in the old sense of the word than in the present one) there appears to be no doubt. What the precise nature of this action is, it would be very hazardous (considering the defective state of our present knowledge of the substance, or com-

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plex of substances of which the wool fibre is composed) to explain. In a former communication I ascribed the lake formation which takes place in the fibre to the action of lanuginic acid. But it appears doubtful whether a sufficient amount of this soluble degradation product could be formed in the fibre to bind the maximum quantities of dyes which are capable of being taken up. It is, however, quite possible, and in my opinion even probable, that other degradation products are formed in the fibre which, while being insoluble, are intermediate again between the substance of the fibre and lanuginic acid, and possess, like the latter, the property of forming lakes.

The fact that the volume of water used in dyeing these acid colours can be varied between wide limits without having any material influence on the amount of colour taken up is *prima facie* evidence that there can be no question here of mere solid solution taking place in the sense attributed to the expression by Witt. That, however, solid solution of the lake may take place in the sense in which I first alluded to it in a discussion on one of my papers I still hold to be probable. According to my conception it would also account for the transparency of the dyed fibre. Besides, the solubility of the colour in water does not appear to bear any relationship to the amount taken up by the fibre, and this would also argue against any pure solution theory.

The new experiments, the results of which are detailed above, relate only to wool. A series of quantitative experiments has, however, also been carried out in my laboratory on the dyeing of cotton with direct colours, the dyestuff having been in most cases estimated both in the bath and directly on the fibre. From these experiments it would appear that the process is not analogous to the dyeing of wool with acid colours, and that it takes place (within certain limits) strictly in accordance with the law of distribution. The work has been considerably retarded in consequence of the difficulty experienced in obtaining chemically pure colours.

AN INTERESTING REACTION OF COPPER SALTS. EDMUND KNECHT. "Memoirs of the Manchester Literary and Philosophical Society," vol. 48. As is well known, the salts derived from titanium sesqui-oxide, Ti_2O_3, are powerful reducing agents. More than fifty years ago, Ebelmen, who was the first to describe the chloride, drew attention to the fact that the aqueous solution of this salt was capable of reducing gold, silver and mercury from their salts, while, according to the same authority, cupric salts are thereby reduced to the cuprous and ferric salts to the ferrous condition; on this latter reaction I have based a method of estimating iron in the ferric condition which is both rapid and accurate. By the addition of titanous chloride to the solution of a cupric salt, I find that in the first instance a reduction takes place in the sense alluded to by

Ebelmen, *i.e.*, cuprous chloride is precipitated, but on adding excess of the titanium solution, the white precipitate is redissolved and after standing for some time, or better still by warming, metallic copper is precipitated. The reaction, which only takes place in presence of considerable excess of the titanous chloride, is, however, incomplete; it is in fact a reversible one, and a method of producing the titanous salt is based upon the action of metallic copper on the tetrachloride. But if titanous sulphate is employed in place of the chloride and the copper solution is not too dilute, instant precipitation of metallic copper takes place, even when the reagent is not added in sufficient amount to form a cuprous salt. By adding excess of the reagent, the whole of the copper comes out as such, presumably according to the scheme :—

$$Ti_2O_3 + CuO = 2TiO_2 + Cu$$
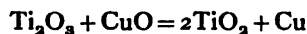
but up to the present I have not been able to verify its correctness quantitatively. Failure in this respect has been partly due to the fact that the precipitated copper is so finely divided that it is found impossible to filter it, while on the other hand its intense colour prevents the use of an indicator in titrating back the excess of titanous sulphate. Moreover, even if it were possible to filter the precipitate, another drawback presents itself, inasmuch as the metal is in such a fine state of division that in contact with the air it is rapidly oxydised and is liable to be partly redissolved by the excess of sulphuric acid which must of necessity be present. In using the reaction as a test for small quantities of copper, this phenomenon accounts for the disappearance of the precipitate after the liquid has been left exposed to the air for some length of time.

With very dilute solutions of copper (one part or less of the metal in 10,000) the reaction with titanous sulphate is not instantaneous, requiring from 2 to 30 minutes for its completion. Under these conditions, it does not in fact show at all at first, but by degrees the solution acquires a dull pink colour, different from that of the titanous sulphate, and only after this the metal makes its appearance. The reaction is best observed by reflected light; transmitted light is of no use, showing only a bluish-green colour when appreciable quantities of the metal are present, and nothing at all in presence of minute quantities. The reaction can be accelerated by the application of heat, but the precipitated metal is never so bright as when operating on cold solutions. In any case boiling should not be resorted to since this will bring down titanic hydrate, which will spoil the delicacy of the reaction. The presence of small quantities of hydrochloric and nitric acids does not mar the reaction, neither is it affected by the presence of the sulphates of metals other than those of the noble metals and of bismuth. Its use as a reagent in group II. is thus precluded.

The limit at which the reaction is visible is, as far as dilution is concerned, one part of copper in one million of water, using a

cylinder of 3in. diameter. As regards the limit in actual weight of metal, this will, of course, depend upon the smallest volume of liquid that it may be convenient to employ, but taking 5 cc. as a basis, the weight of copper which is still clearly discernible is o·ooooi gram (equal to o·ooi per cent. on the gram standard). In using the reaction for the detection of copper in dyed textile fabrics, from one to five grams of the material are incinerated in a small porcelain dish, the ash taken up by dilute nitric acid, and evaporated down on the waterbath with the addition of a few drops of dilute sulphuric acid. The residue is then taken up in a minimum of water and tested as described. Other substances such as tinned vegetables may be similarly examined. The reaction does not lend itself to the estimation of traces of copper by colorimetry, since comparison by transmitted light is useless for small quantities. Even if a means of comparing the precipitates by reflected light (which would involve devising and fitting up of special apparatus) could be devised, it is doubtful whether such a method would take the place of the recognised and more convenient ferrocyanide test.

In conclusion, I may be permitted to draw attention to the remarkable behaviour of an acid solution of titanous chloride towards mercuric chloride. In consequence of the powerful reducing action of the former, one would expect instant precipitation of metallic mercury, but although such precipitation does take place on boiling, no change is noticed in cold solutions beyond the formation of a very slight quantity of crystalline precipitate, the composition of which I have not ascertained. Metallic mercury vigorously shaken with a solution of titanic chloride, yields a small amount of the titanous salt, and the reaction is therefore a reversible one, as in the case of copper, but this fact nevertheless does not explain the non-precipitation of mercuric chloride in the cold.

TITANIUM SALTS AS LABORATORY AGENTS. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1904, No. 4. The first part of the paper relates to a means of estimating indigo by titration with titanous chloride. In the second part of the paper the author draws attention to the usefulness of titanic and titanous salts for the detection of various substances, but mainly colouring matter in dyed fabrics.

ON NAPHTHOL YELLOW S. EDMUND KNECHT and EVA HIBBERT. "Ber. d. Deutschen Chem. Ges." 1904, page 3475. The naphthol yellow which the authors employed was prepared in the usual way by sulphonating and nitrating alpha naphthol, and was purified by repeated crystallisation from concentrated hydrochloric acid. It was found to contain three molecules of water of crystallisation, and forms thin light yellow needles, which are extremely soluble in water. On heating to $100°$ the acid melts in its own water of crystallisation, but solidifies on continued heating to $120°$ to a

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yellow crystalline mass which melts between 140° and 150° to a clear yellow liquid. The free sulphonic acid was found by titration with titanous chloride to contain 99·8% of the compound.

The potassium salt $C_{10}H_4(OK)(SO_3K)(NO_2)_2 + 1\frac{1}{2}H_2O$ was obtained by neutralising the free acid with potassium carbonate, in the form of long, very thin and flexible orange yellow crystals. On heating it becomes intensely red, and at 270° explodes with emission of a violet light. Attempts to prepare a monopotassium salt failed. The sodium salt crystallises with three, the calcium salt with four molecules of water, while the crystallised ammonium salt is anhydrous. The magnesium salt is very soluble in water.

ON SYMMETRICAL TRINITROXYLENOL. EDMUND KNECHT and EVA HIBBERT. "Ber. d. Deutschen Chem. Ges." 1904, page 3477. The authors first prepared synthetical symmetrical xylenol from dimethylhexenon by Knoevenagel's process, and this was converted into the trinitro compound by dissolving in a mixture of ordinary and fuming sulphuric acid on the water bath and then adding to the cooled solution slightly more than the theoretical quantity of nitric acid of specific gravity 1·415. This solution poured into water yielded a precipitate which was filtered off and then dissolved in boiling water. By the addition of potassium chloride, the trinitro compound was separated in the form of its potassium salt. This was then decomposed by boiling dilute hydrochloric acid, from which on cooling the trinitroxylenol separated out in crystals. The analyses agreed with the formula $C_8H_7N_3O_7$.

The compound dyes wool from an acid bath a bright yellow, the shade being somewhat redder than that obtained with picric acid. Towards ammonium sulphide it behave like picric acid, but gives no isopurpuric acid reaction with potassium cyanide, this latter behaviour being borne out by the constitutional formula for isopurpuric acid proposed by Nietzki. The potassium salt was also analysed and was shown to have the composition $C_8H_6N_3O_7K$. A new dinitroxylenol sulphuric acid is also described in the paper.

THE QUANTITATIVE ESTIMATION OF SOME COLOURING MATTERS IN DYED COTTON FABRICS. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," January, 1905, No. 1, vol. xxi. With colours which exhaust the dye-bath completely, we possess a rough means of ascertaining the amount in the fabric by matching the shade on material of the same quality with the particular dyestuff in question. In such cases it is of course a *sine qua non* that the dyestuff employed for matching should either be chemically pure or that we should know its exact composition. But with dyestuffs which do not exhaust the dye-bath, this method is not applicable, and the most important class to which this applies are the so-called direct cotton colours, dyed on cotton.

None of these exhaust the dye-bath, even if the latter is taken as concentrated as possible, and considerable amounts of salt or Glauber salt are added. In order to estimate the exact amount of some of these dyestuffs which is taken up by cotton under fixed conditions, the indirect method has hitherto been usually adopted. This may either be effected by estimating the amount of colour left in the bath colorimetrically, or by preference the absolute amount by titration with titanous chloride[1], when the difference between the amount found and that originally used will give the amount taken up by the fibre. But if the dyestuff is not pure, or its exact composition is not known, the results obtained are only relative and convey but a vague meaning. These methods are naturally of no use if only the dyed fabric is available for analysis, and as the direct estimation of a number of azo-dyes on the fibre appeared to me desirable in a series of experiments which I was carrying out, I began some time ago to look for a suitable method. The first idea which occurred to me was to extract the dyestuff from a known weight of the fabric by means of a neutral solvent, such as dilute alcohol or glycerine, and then to estimate it in the ordinary way by means of titanous chloride. None of the solvents tried sufficed, however, to completely extract the colouring matter. I next tried dissolving the dyed fabric bodily in concentrated sulphuric acid, pouring the solution into water and then titrating with titanous chloride. The results were, however, unsatisfactory, and for a time I abandoned the idea of estimating colouring matters on the fibre by such methods. But not long afterwards, it occurred to me that I had not tried the simplest process of all, viz., titrating the dyed fabric directly with titanous chloride in excess and then titrating back with a ferric salt. A quantitative experiment with Benzo-purpurin 4B showed that the method was workable, as will be apparent from the following figures obtained :—

Colour used ... ... 0·05 grm.
Colour left in solution (by titration)... 0·02257
Colour on fibre ... ... 0·02924 } 0·05181 grm.

This was considered near enough to the amount taken for the result to serve as a working basis. As will be seen further on, the method was found to be not only applicable to benzopurpurin 4B, but also to other azo-dyes of the same series, and it would appear to be generally applicable to those dyestuffs which are destroyed by reduction with titanous chloride.

Simple as the process might appear at first sight, there are certain precautions which must be taken in order to obtain anything like reliable results. The most important of these is the removal of all the active chlorine[2] in the bleached cotton. This may be effected

(1) This Journal, page 243.

2) Most cotton bleached in the ordinary way with bleaching powder contains and tenaciously retains active chlorine. In what form this is held in the bleached material is not known with certainty By using thiosulphate as an " antichlor " it is completely removed.

by steeping for a short period in dilute thiosulphate of soda, afterwards washing in water, or preferably in salt solution to remove any excess of thiosulphate, for the latter, if not removed, would introduce a source of error, as it also uses up titanous chloride. All the bleached cotton yarn used for our experiments was subjected to this treatment previous to being dyed. It was subsequently found, however, that by boiling with dilute hydrochloric acid (1 : 3) for about five minutes practically the same result was brought about. This observation materially simplifies the process. Then again, if there is reason to suppose that ferric iron or copper is present, these require to be removed by treatment with hydrochloric acid. When these precautions are observed the method gives excellent results, which are usually within 2 per cent. of the total amount of colour used or with a 1 per cent. shade within 0·02 per cent. on the weight of the dyed material.

Most of our results were obtained on 5 grms. of cotton, using a $TiCl_3$ solution of such a strength that 1 cc. = about 0·0015 to 0·0017 grms. Fe. We were, however, able to obtain equally good results on 1·5 grms. cotton by using a $TiCl_3$ solution of which 1 cc. = about 0·0003 grms. Fe.

The carrying out of the process is practically the same as that described in our former communication. A weighed quantity of the material is placed in a flask and first boiled with dilute hydrochloric acid. Carbonic acid is then passed in from a small handy generator, and $TiCl_3$ run in. The flask is then heated over a Bunsen until the colour has disappeared, when it is cooled in running water and the excess of $TiCl_3$ estimated by titrating back with standard iron alum solution and KCNS as indicator. The KCNS is added directly to the contents of the flask. During the whole process the CO_2 current must not be interrupted. If the apparatus is in working order a quantitative estimation can be easily carried out in 20 minutes.

The following figures are taken indiscriminately from a very large number of determinations which we have carried out.

BENZOPURPURIN 4B.

Amount of dye taken, 0·1 grm.
Solution ... ... 0·04765 grm.
Fibre ... ... 0·05230 ,,

Total ... ... 0·10000 grm.

Amount of dye taken, 0·125 grm.
Solution ... ... 0·06680 grm.
Fibre ... ... 0·05860 ,,

Total ... ... 0·12540 grm.

CHRYSOPHENINE.[3]

Amount of dye taken, 0.05 grm.

Solution ...	...	0·03655 grm.
Fibre ...	...	0·01372 ,,

Total ...	...	0·05027 grm.

Amount of dye taken, 0·1 grm.

Solution ...	...	0·07310 grm.
Fibre ...	...	0·02610 ,,

Total ...	...	0·09920 grm.

Amount of dye taken, 0·05 grm.

Solution ...	...	0·03622 grm.
Fibre ...	...	0·01399 ,,

Total ...	...	0·05021 grm.

BRILLIANT YELLOW.[4]

Amount of dye taken, 0·05 grm.

Solution ...	...	0·04220 grm.
Fibre ...	...	0·00842 ,,

Total ...	...	0·05062 grm.

ERIKA B.[5]

Amount of dye taken	0·05000 grm.	0·05000 grm.	0·10000 grm.
Solution	... 0·03664 ,,	0·03682 ,,	0·07650 ,,
Fibre ...	... 0·01360 ,,	0·01334 ,,	0·02680 ,,
	0·05024 ,,	0·05016 · ,,	0·10330 ,,

These colouring matters, which may be taken as representative of the direct cotton colours, were all previously obtained in the pure state, and gave on analysis figures which closely approximated to 100 per cent. (See footnotes.) Although we have so far not

(3) The pure dyestuff was prepared in the form of its potassium salt from the commercial article in the following manner :—To the aqueous solution of the commercial dyestuff caustic soda was added in excess. This precipitates the sodium salt but leaves (according to R. Meyer) the mono-ethylether in solution. The product was collected on a vacuum filter, dissolved in water, precipitated with barium chloride, and the barium salt filtered off and washed with hot water. This was then decomposed in presence of alcohol with an amount of sulphuric acid, slightly less than the amount required by theory, and the free colour acid converted into the potassium salt by the addition of potassium acetate. From the hot solution filtered from the barium sulphate, the dyestuff readily crystallises. It forms large lustrous crystals of a rich brown colour, and is not very soluble in water. An analysis yielded the following figures, of which the first is calculated on the formula $C_{30}H_{20}N_4O_8S_2K_2$:—

By titration with $TiCl_3$	... ...	86·56%
Water of crystallisation	... ...	13·20
		99·76

The amount of water of crystallisation found corresponds to 6 mol. (calc. 13·20 per cent).
The aniline salt was found to be quite insoluble in water.

succeeded in obtaining other chemically pure direct colours, I think we may assume that they will behave like these, and can be estimated in the same way.

In examining the derivatives of H acid obtained by combining in alkaline solution, we found that they gave a remarkable reaction after reduction. On exposure to air the decolourised solution turns red owing to the formation of a new, intensely red compound. The same intense red is produced by the addition of iron alum, and I was at first of opinion that this fact would render the estimation of colours like diamine sky blue impossible. Further study of the new colour showed, however, that it was a stable substance, and readily yielded a leuco compound in presence of excess of $TiCl_3$. Its oxidation and reduction were proved to be quantitative on the chemically pure fast acid magenta, and it consequently may serve as indicator in place of sulphocyanide. An estimation of diamine sky blue on the fibre and in the bath, using 0·15 grm. dyestuff, gave the following results :—

Solution	... ...	10·1 cc.	$TiCl_3$
Fibre	... ...	2·5	,,
		12·6	

In a separate experiment 0·15 grm. of the dyestuff titrated in the same way required 12·9 cc. $TiCl_3$.

I am unable to state definite amounts in this case as I have not yet succeeded in preparing chemically pure diamine sky blue. Of the basic colours, I have so far only tried methylene blue. Cotton which had been mordanted with tannic acid and tartar emetic was dyed with 1 per cent. and with ½ per cent. pure methylene blue. The estimation was effected by first heating the dyed material in hydrochloric acid, running in enough titanous chloride to completely decolourise the solution, and the dyed cotton, and then titrating

(4) The Brilliant yellow was obtained as potassium salt from the commercial article by precipitating with barium chloride, and treating the barium salt in about the same way as is described for Chrysophenine. It forms well-defined deep orange-coloured crystals with a metallic sheen. The analysis, based on the formula $C_{26}H_{16}N_4O_9S_2K_2$, yielded :—

By titration with $TiCl_3$	... ...	87·56%
Water of crystallisation	... ...	11·40
		98·96

The amount of water of crystallisation corresponds to 4½ mol. (calc. 11·07 per cent.).

(5) The Erika was prepared as potassium salt as follows :— The commercial product was ground to a paste with conc. sulphuric acid, and after diluting with water the free colour acid was filtered off. These operations were repeated and the free colour acid was converted into the potassium salt and simultaneously precipitated as such by adding potassium carbonate in excess. After filtering on a vacuum filter, the potassium salt was dissolved in water, potassium acetate added, and allowed to crystallise. The separated colour was then washed with alcohol. It forms a heavy crystalline red powder, which yielded the following figures, calculated for $C_{30}H_{19}N_3O_7S_3K_2$:—

By titration with $TiCl_3$	... ...	82·12%
Water of crystallisation	... ...	17·50
		99·62

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back with standard iron alum, until the blue just began to reappear. The following results were obtained :—

Dyestuff used ...	...	0·08450 grm.	0·05000 grm.
Fibre ...	... ...	0·08419 ,,	0·04962 ,,
Solution	... ...	0·00044 ,,	0·00092 ,,
		0·08463 ,,	0·05054 ,,

From this it will be apparent that the method is reliable also in this case. It is my intention to try the process for the estimation of other colours on the fibre.

I have again to acknowledge my indebtedness to Miss Eva Hibbert for her valuable assistance in carrying out the experimental details. In conclusion, I would point out that when acting on mixed shades got with direct colours, the $TiCl_3$, if employed in limited amount, exhibits a remarkable selective action. Thus in greens dyed on cotton with diamine sky blue and chrysamine, chrysophenine, and stilbene yellow C respectively, the yellow was invariably destroyed first, leaving the pure blue on the fibre. In an orange dyed with chrysophenine and benzopurpurin 4B, the yellow was likewise destroyed first, whereas in a violet resulting from benzopurpurin 4B and diamine sky blue the red disappears before the blue. In carrying out these tests, it is, of course, necessary to strictly limit the amount of reagent, otherwise the whole of the colour disappears. A solution of $TiCl_3$, containing 10 cc. of the commercial product and 10 cc. conc. hydrochloric acid per litre, represents a convenient strength for the purpose. I intend to study more closely this selective action, which will not only be useful for the qualitative detection, but may even render possible the rough quantitative estimation of two colours in the same material. Limited oxidation (e.g., with bleaching powder) has a similar selective action on mixed colours.

A SIMPLE TEST FOR PARANITRANILINE RED. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1905, No. 11. This test, which serves to rapidly distinguish paranitraniline red from alizarin red, etc., consists essentially in heating the dyed pattern over a very small gas flame for a few seconds, when the red volatilises and an orange spot suddenly appears where the heat has been applied. The same test can be applied to naphthylamine claret.

THIO-INDIGO RED: A NEW SYNTHETIC DYESTUFF. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1906, No. 5. This consists in the main of a description of a new and interesting dyestuff discovered by P. Friedländer, in which the author deals with the mode of formation and the applications. The pure dyestuff was obtained by the author in a crystallised condition,

and it was shown that after obtaining it in solution by means of fuming sulphuric acid, it can be quantitatively estimated, like indigo, by titration with titanous chloride. The author found that the sulphonic acid could be dyed on wool by the method in general use for acid dyes and yielded good results.

ON THE ACTION OF HUMAN SALIVA ON BLEACHED COTTON. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," July 1905, No. 7, vol. xxi. If a small piece of bleached cotton be placed in the mouth and allowed to remain there saturated with saliva for a few minutes, it does not appear at first sight to have undergone any appreciable change. But if, after having been well washed, the sample is dyed, along with some of the same material untreated, in a direct cotton colour such as benzopurpurin 4B, it will be seen to take up a considerably larger proportion of colouring matter from the bath than the latter. The action of the saliva in thus increasing the colour-receptive properties of the cotton would appear to be very rapid, the difference in shade being strongly marked, even after the first five minutes. After ten minutes the difference in shade is still more apparent, while after twenty minutes the treated cotton takes up in dyeing, at a rough guess, about twice as much colour as the untreated. Similar results were obtained with other direct cotton colours.

The cause of this remarkable phenomenon was not at once apparent. At first I thought it was due to some of the mucus in the saliva becoming fixed on the fibre, but this was disproved by the fact that saliva freed entirely from mucous still showed the same behaviour. Experiments carried out with the various salts contained in the saliva, notably potassium sulphocyanide, showed that these, too, possessed no action, while boiled saliva had lost the characteristic property. From these data, it would be reasonable to infer that the active constituent of the saliva which brings about the change is the ptyaline, an enzyme which is known to possess, as far as starch is concerned, a most powerful hydrolytic action. Of other enzymes, diastase was also found to have some action, but even under the most favourable conditions, it was so slight as to be scarcely appreciable. Possibly other enzymes may exist which equal ptyaline in this respect, and if commercially available, might find employment for the purpose mentioned. So far, the matter is, of course, of purely scientific interest, as far as any treatment of goods in quantity is concerned. The action of saliva might, however, in some cases explain some of the faults in piece goods which dyers so frequently have to contend with. Up to the present I have not had an opportunity of ascertaining whether any chemical or morphological changes occur in the fibre by the treatment, nor have I ascertained how the reaction is affected by varying the source of the saliva, but hope to be able to communicate further on these and other points at a later date.

SOME CONSTITUENTS OF MANCHESTER SOOT. EDMUND KNECHT. "Memoirs of the Manchester Literary and Philosophical Society," vol. xlix., 1905. The coal burnt in Manchester and its immediate surroundings is chiefly what is known as a "fat coal," which, although possessing a high calorific value, is known to yield, especially when used in the household, an abnormally large proportion of smoke and soot. It is to this circumstance that we must ascribe the vitiated condition of the atmosphere in which we exist for the greater part of the year, with its attendant evil effects on the respiratory organs, the desolate appearance of plots of land in the city and its immediate neighbourhood, the dirty condition of all out-of-door objects, the enormous amount of labour involved in keeping the interiors of houses clean, and lastly, to a large extent, the inconvenience experienced by individuals and the trade and commerce of the city caused by such dense black fogs as we experienced last winter.

Having had occasion to examine during February, 1902, some samples of surface snow which had been collected in the centre of the city, and in one of its suburbs, it struck me that it would be of interest if we could obtain some further knowledge of the constituents (more particularly those of organic origin) of the smoky atmosphere we live in, and experiments were undertaken with this end in view, in the carrying out of which I was assisted for a brief period by Mr. Percy Gaunt and by Mr. Cresswell Milnes. It is popularly supposed that the visible products of the incomplete combustion of coal and other fuel consist merely of finely-divided carbon; and this view is frequently supported in works of a scientific or semi-scientific character. There can be no doubt that this view is to a large extent correct in the sense that these visible products contain finely-divided carbon, but that other solid constituents are met with in not inconsiderable amounts in the soot which is deposited from smoke, has been well known for a long time to the manufacturer of carbon blacks.

The manner in which smoke forms from coal burning in our open fire-grates cannot have escaped the attention of even the most casual observer. It will be quite evident from the voluminous disengagement of gases or vapours that in the first instance dry distillation takes place. Where such disengagement is moderate, the vapours take fire and burn with a bright luminous flame; but if the disengagement becomes violent, the vapours either do not burn at all, or only suffer partial combustion, and their bulk finds its way, mixed with a large excess of air, into the chimney. When the first violent disengagement of gas has ceased, the coal burns quietly with a lurid flame, from which no dry distillation products, but only products of incomplete combustion, result. From these considerations I think we may take it that our smoke and soot consist partly of dry distillation products and partly of the products of incomplete combustion, to which must be added the mineral matter,

which is partly volatilised by the heat of the fire, and partly carried away mechanically by the draught.

Our original idea of ascertaining the composition of coal smoke proper presented difficulties which we did not see our way to overcome, so we chose the next best expedient of subjecting ordinary chimney soot to a more exact examination. The first samples examined were taken partly from chimneys in my own house and partly from other chimneys, but were found to vary so much in composition, that it was ultimately decided to obtain an average sample from a dealer, and this subsequently served for all our quantitative experiments.*

In consequence of its constant exposure, while in the chimney, to a current of warm air, this soot may have lost some of its more volatile constituents, and these would in that case have escaped observation. Again, it is quite likely that in one and the same stack the composition of the soot will vary according to the distance from the fire, but this question was not gone into. The methods employed for separating and isolating the constituents were similar to those which are used in the treatment of coal tar. The soot was extracted with boiling dilute sulphuric acid, with the object of removing basic constituents; then with caustic soda, to remove acid constituents and phenols; and lastly with benzene, to extract the hydrocarbons. Modifications of this mode of procedure were also tried, for the sake of convenience. Thus, in one series of experiments, the soot was first extracted with benzene, and the extract, after evaporating off the solvent, treated with sulphuric acid and then with caustic soda. In another case the soot was extracted with benzene, and this extract was treated with caustic soda only (previous experience having shown that practically none of the basic constituents were taken out by the benzene). The benzene extract was separated from the soda lye, and from the black tar which formed a middle layer, and in this case was the only portion further worked on.

Aqueous extract. In all the samples of Manchester soot which came under examination, it was found that the aqueous extract showed a strongly acid reaction, due to the presence of free sulphuric acid, which amounted on an average to about one per cent.† The aqueous extract contains practically all the ammonia and pyridine bases. By a tedious process of extraction, I succeeded in isolating from it both ammonium sulphate and ammonium chloride by purely mechanical means.

* A large proportion of the household soot collected in Manchester is sold to dealers, who in their turn dispose of it for agricultural or horticultural purposes. I am informed that some is sold locally, but that the bulk goes to Kent, where it is used as a manure for hops. Its effective constituent as a manure consists of salts of ammonia. At the same time, however, it acts as an insecticide, and this property is possibly due to the presence of pyridine and allied bases. At any rate it is certain that its value as a manure cannot depend altogether upon the amount of ammonia it contains, as its price (3s. per cwt.) would be far too high in proportion to the percentage (10·15) of the latter.

† A sample of soot which came from a suburb of London (E.) also yielded a strongly acid aqueous extract, whereas a sample which I obtained from Prague (lignite coal) gave an extract which was neutral to litmus paper.

Sulphuric acid extract. 500 grms. soot were boiled for several hours with 4 litres dilute sulphuric acid, filtered, washed, and the united filtrates evaporated down to a quarter of the original bulk. A considerable quantity of a crystalline deposit thus separated, amounting to 9·5 grms. This was found on examination to consist of an impure calcium sulphate. It is noteworthy that the same deposit was obtained with all the Manchester samples worked on as well as with the Prague sample. It might have been taken for granted that the presence of calcium sulphate was due to the action of the sulphuric acid on the mortar in the chimneys, but the occurrence of this substance in surface snow would appear to indicate that the lime had come out of the coal. The filtrate from the calcium sulphate was of a clear light brown colour, and was found on analysis to contain ammonia equivalent to 10·7% ammonium sulphate on the weight of the original soot. This extract was not further examined.

Caustic soda extract. 1000 grms. soot were extracted as before with boiling dilute sulphuric acid and washed. The residue was then boiled for three hours with eight litres water and 200 grms. caustic soda. A dark brown liquid resulted, which was filtered off, and the acid constituents precipitated by acidulating with dilute sulphuric acid. The product thus obtained amounted to 109 grms. It was of a rich brown colour, and possessed a strong sooty smell. On heating it neither melts nor volatilises, but simply chars with evolution of but little gas. It resists nitration and sulphonation, and is soluble in boiling sodium carbonate. The solution in caustic soda is not precipitated by carbonic acid. In its general properties the substance (which is nitrogenous) would appear to resemble some of those indefinite brown organic substances which are classed as humic acid.[*] A portion of the caustic soda extract, melted in the well-known manner with sodium sulphide, yielded a sulphide colour which resembles in its tinctorial properties the best brands of Cachou de Laval, and dyes cotton in absolutely fast shades from a light fawn to a brown black, according to the amount of colour employed.

Benzene extract. The residue from the caustic soda extract was dried and then extracted with hot benzene. The solvent assumes a deep brown colour, and the extraction is soon complete. After evaporating off the benzene, a greasy, almost black, residue, was obtained, amounting to 13% by weight of the original soot. It is sticky, and possesses the consistency of butter at the ordinary temperature, but readily softens on warming. When heated, it froths and burns with a smoky flame. For further treatment, the product was gently heated until the frothing had ceased, when it solidified on cooling to a brittle black shining mass. This was then rapidly distilled from a glass retort, and the distillate collected in

[*] According to Köhler (" Die Fabrikation des Russes," p. 13) a brown pigment known as "bistre" was formerly prepared from the soot which separated as a glossy black coating near the fire.

two portions. The first of these, amounting to 28 grms., formed a clear brown oil, the second, amounting to 6 grms., a light reddish-coloured very thick fluid, which sets at once on cooling. The first distillate, after standing for some time at a low temperature, became semi-solid, owing to the separation of crystals, which were filtered off and purified by recrystallising several times from boiling absolute alcohol. The substance was thus obtained as a mass of interlaced, beautiful silver-white crystals, which showed a constant melting point of $59 \cdot 5^\circ$. The crystals being soft, their beautiful appearance is spoiled by handling. As the yield only amounted to $0 \cdot 294$ grm., it was not possible to go very deeply into means of identification. The substance dissolved in carbon tetrachloride does not discolourise a dilute solution of bromine in the same solvent. It is slightly soluble in boiling alcohol, but practically insoluble in the cold. Furthermore it appears to resist nitration and sulphonation. The mean of two combustions yielded the following figures :—

$$
\begin{array}{lll}
\text{C.} & \ldots \quad \ldots \quad \ldots & 84 \cdot 8\% \\
\text{H.} & \ldots \quad \ldots \quad \ldots & 14 \cdot 1\% \\
\hline
& & 98 \cdot 9\%
\end{array}
$$

From these data it would appear probable that the substance is a saturated hydrocarbon of the paraffin series, and from its melting point and appearance it might be inferred that it is probably identical with the Heptacosane $C_{27}H_{56}$ (m.p. $59 \cdot 5^\circ$) which Schwalb* isolated from beeswax. The filtrate from this characteristic crystalline substance showed a sp. gr. of $1 \cdot 056$ at 15°. It was subjected to distillation in a partial vacuum (80 mm. pressure). It began to distil at 70°, and the temperature gradually rose to 285°, when it went up suddenly to 305°. At this point the distillate began to thicken, the thermometer slowly rising to 340°, and then suddenly to 400°, when practically all had passed over, and the operation was stopped. The resulting thick, brown oil, amounting to $18 \cdot 5$ grms., was soluble in alcohol, ether, benzene, and glacial acetic acid. The second part of the distillate was not sufficient in amount to allow of a more careful examination. Its solution in benzene and in alcohol shows a characteristic intense green fluorescence. From the alcoholic solution I succeeded in isolating a very small quantity of beautiful sulphur yellow crystals.

It is evident from the behaviour of the benzene extract in distilling that it consists mainly of hydrocarbons of high boiling points. As these range in the first distillate from 170° to 400° (at 80 mm.), it would further appear probable that they represent a complex mixture.

Soot after extraction. After extracting successively with acid alkali and benzene, the soot, though much darker than before

* "Lieb. Ann.", 235, p. 117.

extraction, still showed a brownish-black colour, which is possibly due to the considerable amount of ash which it contains (the original sample contained 19% of a red-brown ash). In this condition it is extremely inflammable, in fact it takes fire spontaneously at a temperature of about 100°, and is then difficult to extinguish. A large plate, containing the extracted soot taken from the drying stove, was seen to contain a little glowing carbon at one point, and this was extinguished. After a short time, however, it began to glow in a different part, and this being also extinguished, another part took fire, and so on, until it was nearly cold. The following table gives the amounts of constituents estimated directly :—

Ammonium sulphate	10·7%
Mineral matter (ash)	19·6%
Acid constituents	10·9%
Benzene extract (hydrocarbons) ...	13·0%
Difference (carbon?)	45·8%
	100·0%

The sample of London soot alluded to above was found to contain considerably less extractive matter than the Manchester sample. The difference was especially noticeable in the case of the benzene extract, which in the London sample only amounted to 1·3%.

A sample of soot from Prague, for which I am indebted to Dr. F. Rademacher, showed that the products of the incomplete combustion of their lignite coal are of a very different character. The soot, which is of a brown colour, gave an aqueous extract which was neutral to litmus paper. On evaporating down the solution, calcium sulphate separated out in almost colourless crystals. The acid extract contains only traces of ammonia. Of acid constituents soluble in caustic soda I found 2%, while the benzene extract only amounted to 0·2%.

From the brief and incomplete account which I have brought before you, it is at least evident that the composition of Manchester soot is more complicated than is usually imagined. The cause of one of its most characteristic properties, viz., its disagreeable smell, I was unable to trace. It has been ascribed to pyridine bases, but I do not know on what experimental basis this assumption is made. Certain it is that it pervaded all the various products which were isolated, and is even possessed by the recrystallised colourless hydrocarbon which was obtained from the benzene extract. To my mind, the smell is more akin to humus or to the peculiar odour which is given off from the earth when a shower of rain falls after a period of dry weather, than to that of pyridine. It would be interesting if one could ascertain what proportion of the solid matter contained in smoke is retained by the walls of the chimney as soot, and what proportion enters the atmosphere. This would of course depend largely on the conditions, such as quality of coal, construction of

the hearth or grate, length and width of stack, and to a certain extent whether the chimney had been recently swept or not. In any case, however, I should be inclined to say that in a household fire by far the greater portion of the solid particles enters the atmosphere, and that the accumulated soot consequently only represents a comparatively small proportion of the separated matter. When high winds prevail, the smoke in the city is carried away so rapidly that its presence is not felt, but with a still atmosphere or a gentle air it falls to the ground, where its presence is best revealed by the appearance of snow which has been lying for some days. Though this is blackest in the city itself, its colour shows that deposition takes place for many miles round Manchester, and it cannot but be that this deposition must exert some influence on plant life. With a clayey or sandy soil, which is not manured or limed, there is nothing to neutralise the free sulphuric acid in which our atmosphere has been shown to abound by various observers, and it is to this circumstance mainly that its destructive action on vegetation must be ascribed. To suggest a remedy would here be out of place, for it would open up the whole question of smoke abatement in dwellings. It is common knowledge that the average household grate is capable of considerable improvement, as far as efficiency is concerned, but with the coal which is available in this district, no material improvement in the atmosphere can be looked for without some legislation in this respect.

THE ANALYSIS OF INDIGO. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1906, No. 11. This paper is controversial in character, and is written with the object of meeting and disarming the adverse criticisms which W. P. Bloxam ("Journal of the Society of Chemical Industry," 1906, p. 736) had advanced disparaging the author's method of estimating indigotin by titration with titanous chloride. The author, after repeating much of his previous work and adducing further experimental evidence in favour of the correctness of his original method, concludes that Bloxam's criticisms, as far as they relate to this method, were not justified.
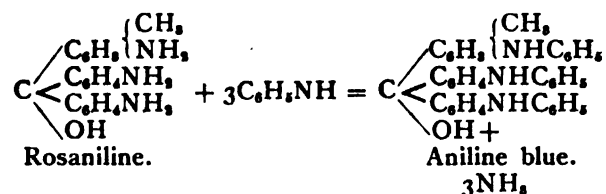
ON THE CHLORINATION OF WOOL. EDMUND KNECHT. "Journal of the Society of Dyers and Colourists," 1906, No. 12. The author points out that he (in conjunction with E. E. Milnes) had anticipated the recent work of Vignon and Mollard on the chlorination of wool ("Rév. gén. des mat. col." 1906, p. 226) fourteen years previously (see "Journal of the Society of Chemical Industry," 1892, p. 115). The author also criticises a publication of M. Grandmougin ("Zeitsch. f. Farben. Ind." 1906, p. 397) on the same subject.

THE COMPOSITION OF ANILINE BLUE. EDMUND KNECHT. ("Journal of the Society of Dyers and Colourists," April, 1907, No. 4, vol. 23). Aniline Blue is obtained, as is well known, by heating pure Rosaniline base with a large excess of aniline oil and a

little benzoic acid for periods varying from two to four hours to a temperature of about 180°. A considerable amount of ammonia is given off during the process, and it has until recently been assumed that the formation of the blue (in its purest form) may be represented by the following equation :—

$$C\begin{cases}C_6H_2\begin{cases}CH_3\\NH_2\end{cases}\\C_6H_4NH_2\\C_6H_4NH_2\\OH\end{cases} + 3C_6H_5NH = C\begin{cases}C_6H_2\begin{cases}CH_3\\NHC_6H_5\end{cases}\\C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\\OH +\end{cases}$$

Rosaniline.　　　　　　　　Aniline blue.

$$3NH_3$$

Aniline Blue or Rosaniline Blue was accordingly regarded as the triphenylated Rosaniline. In 1904, however, Baeyer and Villiger[*] concluded from the results of an elaborate investigation into the subject, that the Aniline Blue of commerce consists of almost pure diphenylated Rosaniline.

In a paper read before the Society of Dyers and Colourists in November, 1905[†], I described a method for the volumetric estimation of a number of colouring matters which yield colourless leuco compounds, and among these Spirit Blue was included. I stated at the time that the crystallised commercial products yielded (after sulphonating) on titrating with $TiCl_3$, results which did not by any means agree with theory, but that two samples of blue which had been prepared in the laboratory from pure Pararosaniline yielded by the same treatment almost theoretical results, and were found to contain nitrogen equivalent to the amount contained in triphenyl-pararosaniline. In view of the fact that all the other dyestuffs which we had analysed by the reduction process gave, when in the pure state, almost theoretical figures, and that our phenylated rosanilines behaved in the same way and showed besides correct nitrogen values, I was not prepared to accept unconditionally these findings of Baeyer and Villiger, and allowed the matter to drop for the time being, with the object of carrying out a further investigation which might lead to a satisfactory explanation. Having other matters in hand I did not, however, proceed any further at the time, and have now been anticipated by Lambrecht, who in a recent communication[‡] offers a perfectly satisfactory solution of the difficulty. It had been previously generally assumed that Pararosaniline
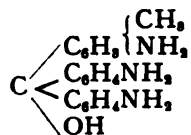
$$C\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH_2\\OH\end{cases}$$
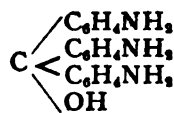
[*] " Berl. Ber.", 1904, p. 2870.
[†] This Journal, page 253.
[‡] ' Berl. Ber.", 1907, p. 247. See also " Journal of the Society of Dyers and Colourists," 1907, p. 125.

and its homologue, Rosaniline—

$$C \begin{cases} C_6H_3 \begin{cases} CH_3 \\ NH_2 \end{cases} \\ C_6H_4NH_2 \\ C_6H_4NH_2 \\ OH \end{cases}$$

behave similarly in phenylating. Lambrecht has, however, shown that in the Rosaniline, the methyl group (from the orthotoluidine contained in the oil for red) which occupies the ortho position in relation to the amido group, presents a steric resistance (hindrance) to the entrance of a phenyl group into the latter, and this bears out the statement of Baeyer and Villiger that diphenyl rosaniline represents the most highly phenylated product that can be obtained by the action of aniline on Rosaniline. On the other hand, Lambrecht was able to obtain from phenylated Pararosaniline the identical triphenylparaleucaniline which Baeyer and Villiger had obtained by a roundabout process, thus showing that Pararosaniline is capable of taking up three phenyl groups. A further proof of the composition of the ordinary Rosaniline Blue is afforded by the yield obtained in its preparation on a large scale, which agrees, according to private information which I have obtained from two independent sources, with diphenylrosaniline.

The triphenylpararosaniline which served for our experiments was prepared by boiling pure crystallised pararosaniline (1 pt.) with a large excess (10 pts.) of pure, freshly-distilled aniline for three hours in presence of some benzoic acid. The resulting melt was treated with excess of hydrochloric acid and the precipitated hydrochloride . of the blue was washed with boiling water, and then recrystallised from alcohol. A nitrogen estimation by the Kjeldahl method gave :— 7·38 per cent., Calc. for $C_{37}H_{30}N_3Cl$. 7·6 per cent. on the dry substance. One grm. was sulphonated by heating for one hour with conc. H_2SO_4 to 100°. The product was poured into water and made up to 250 cc. Of this 50 cc. were titrated with $TiCl_3$ in presence of 20 cc. of a 20 per cent. solution of Rochelle salt in the same way as described in my paper :—1 cc. $TiCl_3 = 0·00147$ gr. Fe., 50 cc. required 12·9 cc. $TiCl_3$; and since 551·5 grms. Triphenyl-pararosaniline = 112 grms. Fe., we have 0·09337 grms. Triphenyl-pararosaniline in 50 cc. = 93·37 per cent., moisture = 6·89 per cent. ; total = 100·17 per cent. Another sample prepared in the same way gave 7·35 per cent. N, and 99·4 per cent. colour. It is thus evident that titration with $TiCl_3$ gives accurate results with triphenyl-pararosaniline hydrochloride, but before the method can be extended to the valuation of technical Aniline Blues and their sulphuric acids (Alkali Blues, Soluble Blues) further work will be necessary in order to ascertain what relation the shade bears to the degree of phenylation.

THE DISTRIBUTION OF ACID AND BASE IN THE DYEING OF WOOL WITH CRYSTAL SCARLET. EDMUND KNECHT. ("Journal of the Society of Dyers and Colourists," September, 1907, No. 9, vol. 23.) It is well known that in the dyeing of wool with basic dyes like Magenta and Crystal Violet the acid constituent of the dyestuff remains quantitatively in solution, the base only entering into combination with the fibre to form an insoluble coloured compound. In the dyeing of wool with acid dyes, Gnehm showed that if the benzidine salt of Naphthol Yellow is used as the dyestuff, the benzidine remains quantitatively in the bath, but no experimental data have hitherto been available to show how acid and base are distributed in dyeing when a compound of the acid dyestuff with an inorganic base is used. This is, indeed, not astonishing if we take into account the difficulties which would be presented by the problem if the dyestuffs were used in their ordinary commercial condition, viz., as sodium salts, containing variable amounts of common salt and Glauber's salt. But even if the sodium salt were used in the chemically pure state, the low percentage of the sodium (an exact estimation of which is not in any case an easy matter), coupled with the unavoidable presence of inorganic substances, including sodium and potassium compounds, in the relatively large mass of wool which it is necessary to use for the experiment, must make it extremely difficult to obtain reliable results. By employing the magnesium salt of an acid dye these difficulties are, however, overcome, the separation of magnesia from the other bases and its gravimetric estimation being readily accomplished. Furthermore, the magnesium salts of the ordinary acid dyes are sufficiently soluble, and the magnesium sulphate resulting from the double decomposition of the dye-salt and the sulphuric acid in the dye-bath is also readily soluble in water. As dyestuff, Crystal Scarlet was chosen, since it yields a sufficiently soluble magnesium salt, which can be easily obtained in the pure state. This was prepared by mixing hot solutions of ordinary Crystal Scarlet and magnesium sulphate, and allowing to cool, when the magnesium salt separates in the form of beautiful lustrous crystals. The product was purified by recrystallisation, and yielded on analysis the following figures :—

Colour by titration with $TiCl_3$	74·96%
Water at 200°	24·60%
	99·56%

A gravimetric estimation of the magnesium as pyrophosphate yielded 3·80 per cent., as against 3·75 per cent., the amount calculated for 74·96 per cent. colour.

Ten grammes of purified loose wool were dyed with an amount of the crystallised dyestuff corresponding to one gramme of pure colour. The dye-bath was acidulated with 3 grms. sulphuric acid, made up to one litre, and the dyeing conducted for one hour at the boil.

After dyeing, the bath was found to be almost exhausted, the amount of colour remaining in solution being only o·01513 grm., or a little over 1½ per cent. of the colour employed. A gravimetric estimation of the magnesium in the bath gave (after deducting the amount extracted from the same weight of wool by sulphuric acid alone under conditions identical with the dyeing experiment) o·0498 grm., which agrees very closely for the amount calculated for one gramme of pure colour, viz., o·0499 grm. It is thus evident that under the conditions of the experiment the whole of the base remained in the dye-bath. That, however, it is still present in combination with the colour acid before the dyeing commences, in spite of the presence of such a large excess of sulphuric acid, is evident from the appearance of the cold dye-bath, which is filled with crystals. These dissolve completely on heating, so that the dyeing proceeds normally, but if the solution is cooled they separate out again. On mixing the pure magnesium salt with three times its weight of sulphuric acid in more concentrated solution, about 90 per cent. was found to separate out from the hot solution on cooling in an unchanged condition.

It is not improbable that the sodium salts of Crystal Scarlet and of other acid dyes behave similarly in dyeing, and the mechanism of the process might be explained by the following cycle of changes.

In the first instance the effect of the boiling dilute acid is to impart to the wool the necessary affinity for the dyestuff. The relatively small amount of colour acid which is liberated by the excess of sulphuric acid is then taken up by the fibre, with which it forms an insoluble lake, and the equilibrium being disturbed, more of the salt is decomposed, and so on until the reaction becomes practically complete.

A DELICATE TEST FOR TITANIUM. EDMUND KNECHT. ("Chemiker Zeitung," 1907, No. 51.) The new test is based upon the decolourising action which titanous chloride has on many dye-stuffs. In testing for titanium in a mineral or ash, the author proceeds as follows :—After fusing in the ordinary way with soda or fusion mixture, the cooled melt is acidulated with hydrochloric acid and the mass evaporated to dryness on the water bath. The residue is taken up with dilute hydrochloric acid, and the silica and titanic oxide, which are insoluble, collected on a filter. The mixture of silica and titanic oxide is then warmed in a small test tube with hydrochloric acid (1 : 1) and a small piece of zinc foil, and allowed to stand. If titanium is present it will be reduced to titanous chloride, which will decolourise a dilute solution of indigo carmine in presence of Rochelle salt on warming. Methylene blue is better for the purpose than Indigo carmine, but in using it no Rochelle salt must be added. By this reaction it is possible to detect as little as o·00001 grm. of titanium.

THE ALKYL COMPOUNDS OF GOLD. WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON. ("Transactions of the Chemical Society," 1907, vol. 91, p. 2061.) According to Mendeléeff's original conception of the periodic classification of the elements (Annalen, 1871, Supp. Bd. 8, 151), it had been concluded that elements occurring in the higher even-numbered series do not yield stable alkyl compounds, and that if alkyl compounds were obtainable they would be totally different in properties from previously known organo-metallic substances. The discovery by the authors of diethylauric bromide—$(C_2H_5)_2AuBr$—which is prepared by the action of magnesium ethyl bromide in ethereal solution on either auric chloride or bromide does not verify this view. The compound crystallises in long colourless doubly-refracting needles, which melt at 58°, and decompose explosively at about 70°. It is insoluble in water, but soluble in the ordinary organic solvents. When diethyl-auric bromide is dissolved in warm aqueous ammonia and the solution allowed to evaporate in a vacuum over sulphuric acid, aminodiethylauric bromide is obtained. This substance may be recrystallised from benzene, and it has the composition $(C_2H_5)_2AuBr.NH_3$. Monoethylauric dibromide—$(C_2H_5)AuBr_2$—is prepared by adding a dilute solution of bromine in chloroform to a solution of an equimolecular proportion of diethylauric bromide in the same solvent and allowing the mixture to stand at the ordinary temperature. After recrystallising from chloroform, monoethylauric dibromide yields dark ruby red prisms which decompose gradually without melting. The difficulties of the work are rendered considerable on account of the small yields obtained in the preparation of diethylauric bromide. It will be perceived that the compounds described resemble other alkyl compounds, especially those of tin and thallium, and that additional interest lies in the fact that they verify the trivalency of gold.

A NEW CLASS OF ORGANO-TIN COMPOUNDS CONTAINING HALOGENS. WILLIAM J. POPE and STANLEY J. PEACHEY. ("Proceedings of the Royal Society," vol. 72, 1903, pp. 7-10). Most of the organo-tin compounds which have hitherto been described may be regarded as derived from the hypothetical stanni-methane, SnH_4, and adopting a nomeclature based upon the name of this substance, the simple types of known organo-tin compounds may be described as the tetralkylstannimethanes, the trialkylstanni-methyl chlorides, bromides and iodides, and the dialkylstanni-methylene chlorides, bromides and iodides. The analogy between the various classes of derivatives of stannimethane and of methane is as yet incomplete, in that no organo-tin compounds corresponding in constitution to chloroform, bromoform and iodoform have been described. Methods for preparing such derivatives are, however, given in the present paper, so that the analogy of constitution existing between the corresponding classes of alkyl and halogen

compounds of carbon and tin is shown to be complete, and of the kind illustrated in the following table :—

$C(CH_3)_4$.	Tetramethylmethane	$Sn (Ch_3)_4$.	Tetramethylstan-
$C(CH_3)_3I$.	Trimethylmethyl-iodide	$Sn(CH_3)_3I$.	nimethylmethane Trimethylstanni-methyliodide
$C(CH_3)_2I_2$.	Dimethylmethylene iodide	$Sn(CH_3)_2I_2$.	Dimethylstanni-methylene iodide
$C(CH_3)I_3$	Methyliodoform	$Sn(CH_3)I_3$.	Methylstanniodo-form
CI_4.	Carbon tetraidoide	SnI_4.	Stannic iodide
$CH_3CO.OH$.	Acetic acid	$CH_3SnO.OH$.	Methylstannoxylic acid

Methylstanniodoform, CH_3SnI_3, is obtained by warming a mixture of tetramethylstannimethane (two parts) and stannic iodide (seven parts) on the water bath; a clear solution is obtained which, after standing for a few hours at the ordinary temperature, deposits the new compound in large straw-coloured needles melting at 82° to 84°. It is odourless, and dissolves readily in alcohol, acetone and benzene. Alkaline hydrolysis converts it into methylstannoxylic acid.

Methylstannibromoform, CH_3SnBr_3, is formed when methylstan-noxylic acid is dissolved in concentrated hydrobromic acid. By extracting the solution with light petroleum and evaporating the solvent, the compound is obtained in the form of long colourless prisms, which melt at 50° to 55°, and may be distilled without decomposition.

Methylstannichloroform, CH_3SnCl_3, is conveniently prepared by gently warming methylstannoxylic acid in a current of dry hydrogen chloride. A vigorous reaction occurs and methylstannichloroform distils, condensing in the receiver in long colourless prisms, melting at 105° to 107° and distilling without decomposition at 179° to 180°.

PREPARATION OF THE TETRALKYL COMPOUNDS OF STANIMETHANE. WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY. " Proceedings of the Chemical Society," vol. 19, December, 1903. The authors show that the tin tetralkyls may be advantageously prepared by the aid of Grignard's reaction. Stannic chloride reacts vigorously with an ethereal solution of magnesium methyl iodide, giving an almost theoretical yield of tin tetramethyl. A number of mixed alkyl compounds have been prepared and examined.

THE RESOLUTION OF EXTERNALLY COMPENSATED DIHYDRO-α-METHYL INDOLE. WILLIAM JACKSON POPE and GEORGE CLARKE, JUNR. " Journal of the Chemical Society," vol. 85,

1904. The authors have succeeded in resolving externally compensated dihydro-α-methylindole by combining the base with d-bromocamphorsulphonic acid, whereby l-dihydro-α-methylindole d-bromocamphorsulphonate is obtained as the least soluble salt.

THE RESOLUTION OF TETRAHYDRO-P-TOLUQUINALDINE INTO ITS OPTICALLY ACTIVE COMPONENTS.

WILLIAM JACKSON POPE and THOMAS CONSTANTINE BECK. "Journal of the Chemical Society," vol. 91, 1907. The resolution of externally compensated tetrahydro-p-toluquinaldine is effected by treating the base with the d-αβ-bromocamphorsulphonic acid of Armstrong and Lowry. It is thus shown that this acid may be added to the list of those available for the resolution of dl-bases.

A NEW CLASS OF ORGANO-METALLIC COMPOUNDS: TRIMETHYLPLATINIMETHYL HYDROXIDE AND ITS SALTS.

WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY. "Proceedings of the Chemical Society," vol. 23, No. 323, 1907. The authors describe the preparation, by the use of Grignard's reaction, of the hitherto unknown alkylplatinic halides. Trimethylplatinimethyl iodide, $(CH_3)_3PtI$, is formed by the action of platinic chloride dissolved in ether on magnesium methyliodide. Silver hydroxide converts the iodide into trimethylplatinimethyl hydroxide, $(CH_3)_3PtOH$, from which substance the nitrate, chloride, bromide and cyanide of the base are readily prepared.

A DEVELOPMENT OF THE ATOMIC THEORY WHICH CORRELATES CHEMICAL AND CRYSTALLINE STRUCTURE AND LEADS TO A DEMONSTRATION OF THE NATURE OF VALENCY.

WILLIAM BARLOW and WILLIAM JACKSON POPE. ("Transactions of the Chemical Society," 1906, 89, pp. 1675-1744.) Starting with three assumptions regarding the nature of the chemical atom, the chemical molecule, and a crystal, the authors proceed to build up close-packed assemblages of spheres corresponding to different chemical compounds, and to study the partitionings of them which can be effected. The method may be checked to a large extent quantitatively by reference to the crystallographic measurements of the compounds. Since the assemblage itself can be partitioned into units identical in composition, configuration, and shape with the chemical molecule, the study of this partitioning at once reveals a number of important geometrical properties of the molecule. Many of these properties furnish immediate explanation of observed peculiarities of chemical behaviour, such as those relating to isodynamic compounds and to substitution in aromatic nuclei.

By studying the close-packed assemblages which represent related compounds and the methods of their conversion into each other, it is found that the atoms of the elements must be represented by

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spheres of influence directly proportional to their fundamental valencies. The ordinary law of valency is thus merely an interpretation of a simple geometrical property of close-packed homogeneous assemblages of spheres; the other aspects of valency, e.g. multivalency, are also traceable to simple geometrical properties of such assemblages. The spheres of atomic influence of equivalent atoms are only approximately the same, and it follows that differences exhibited between the types of combination effected between two given elements at different temperatures may be traced to slight differences in the relative rate of increase of the volumes of the atomic spheres of influence as the temperature rises. The absolute magnitude of the sphere of atomic influence of an element may change considerably in different compounds, although the relative magnitudes are but slightly affected.

In the discussion of relationships between crystalline form and molecular constitution use has been made of the "equivalence parameters" for the determination of molecular dimensions. In this way the connections between related substances are more clearly emphasised than has hitherto been possible with the use of ordinary axial ratios, or of topic axes. Illustrative of the methods of investigation close-packed assemblages have been derived which represent entirely the known chemical and crystallographic data of benzene, triphenylmethane, naphthalene, anthracene, and some of their derivatives.

THE RELATION BETWEEN THE CRYSTALLINE FORM AND THE CHEMICAL CONSTITUTION OF SIMPLE INORGANIC SUBSTANCES. WILLIAM BARLOW and WILLIAM JACKSON POPE.

("Transactions of the Chemical Society," 1907, 91, pp. 1150-1214.) Only two simple homogeneous close-packed assemblages of equal spheres exist, one of which possesses holohedral cubic symmetry, and the other holohedral hexagonal symmetry; and that some 85 per cent. of the elements crystallise in either the cubic or hexagonal systems is naturally considered in connection with this geometrical fact. The relationship of the crystalline forms of the elements which belong neither to the cubic nor to the hexagonal systems are explained by the supposition that the atoms of these elements are not exactly of the same size, and consequently a degradation of the symmetry takes place. This conclusion is amply verified by referring to known geometrical data in these cases, and the crystalline forms of sulphur, iodine, and tin are successfully deduced in accordance with the principles laid down in the paper. It is also shown that the complex crystalline properties of the binary compounds containing elements of equal valency, e.g. the halide salts of the alkali metals are in harmony with the representative homogeoneus assemblages derived from the closest-packed cubic arrangement of equal spheres. The treatment of assemblages representative of the trihalogen salts of the alkali metals is specially

interesting, as the comparison of the equivalence parameters leads to conclusions as to the relative sizes of the spheres of influence, and hence of valency values of elements in the same group; for instance, the sphere of atomic influence of iodine is the largest, and that of fluorine the smallest among the halogens.

ON POLYMORPHISM, WITH ESPECIAL REFERENCE TO SODIUM NITRATE AND CALCIUM CARBONATE. WILLIAM BARLOW and WILLIAM JACKSON POPE. ("Transactions of the Chemical Society," 1908, 93, pp. 1528-1560.) In the terminology adopted by the authors, polymorphism may be defined as the existence of two or more close-packed assemblages, distinguished by difference of marshalling, all of which are partitionable into units or chemical molecules of practically identical configuration. Numerous cases are quoted in which the goniometric constants for two polymorphously related substances can be immediately referred to practically the same set of axial ratios. By the construction of assemblages of spheres representing a pair of polymorphously related substances, e.g. sodium and potassium nitrates, which substances are further related by the second geometrical property (defined in the paper on page 370) to the two polymorphously related modifications of calcium carbonate, the conclusion is drawn that where the above dimensional coincidences obtain as between two assemblages, the latter are composed of practically identical layers or blocks of the aggregated spheres of atomic influence. The method of treatment, which is highly successful, is subjected to the crucial test in that many data are available concerning the crystal structure of the substances discussed.

THE CONSTANTS OF BOG BUTTER, FOUND IN THE PEAT IN IRELAND. L. G. RADCLIFFE and W. H. MADDOCKS. ("Journal of the Society of Chemical Industry," January, 1907.) A determination of the constants of a sample of butter some hundreds of years old found buried in the peat, of interest as showing the change that a fat like butter undergoes when immersed for centuries in peat water.

A REDETERMINATION OF THE CONSTANTS OF CAR-NAÜBA WAX. L. G. RADCLIFFE. ("Journal of the Society of Chemical Industry," February, 1906.) A series of figures obtained by the examination of a sample of genuine Ceará wax.

ESTIMATION OF COPPER BY TITANIUM TRICHLORIDE. EZRA LOBB RHEAD. ("Transactions of the Chemical Society," 1896, p. 1491.) The method of estimating copper described in this paper consists in reducing an acid solution of a cupric salt to which potassium thiocyanate has been added by means of titanium trichloride, a powerful reducing agent introduced by Knecht in 1903 ("Ber.",

36, 166, 1549). The behaviour of the solution is somewhat peculiar. Cupric thiocyanate is formed, but remains in solution, forming a brownish-coloured liquid. On adding pure titanium trichloride to the solution this colour is discharged, cuprous thiocyanate being precipitated, and a colourless, or nearly colourless, solution remains. The end reaction is reached too gradually to be easily distinguished. If, however, a ferric salt be added to the solution, a deep red colouration is produced with the excess of thiocyanate and persists until the whole of the copper salt has been reduced to the cuprous state and precipitated. The red colouration is ultimately discharged by excess of titanium trichloride, showing that under the conditions of the experiment the copper was first affected.

Experiment showed that ferrous salts reduce cupric salts to the cuprous state very readily in acid solutions, and the amount of the reagent consumed was the same with or without the addition of ferrous compounds; the quantity of titanium trichloride required to reduce the ferric salt resulting from the oxidation of the ferrous by the cupric salt is identical with that required to reduce the corresponding quantity of the latter. The determination of the end of the reaction was thus rendered very easy, the red colour of iron thiocyanate being so pronounced. The end reaction is as sharp as in titrations with permanganate, a single drop of a weak solution being sufficient to determine it. The addition of the ferrous iron may be made to the solution of copper or to the standard titanium trichloride solution. In the latter case, the addition of the reagent causes an increase in the depth of colour in the copper solution until near the end, owing to the increase in the amount of iron added with the reagent. This method of adding iron is somewhat less convenient, but ensures the whole of it being present in the ferrous state, since it is mixed with the reducing agent. It interferes, however, with the cross standardisation by means of iron, since ferrous salts reduce cupric salts. If, however, the solution be standardised with pure copper, no difficulty is encountered, and the use of two solutions is avoided. There is also an objection to adding iron to the reagent in estimating small quantities of copper and in very dilute solutions, as so little iron may be added as to render the end reaction indistinct It is, therefore, better in most cases to use pure titanium trichloride and add a ferrous salt to the copper solution. At present the commercial titanium salt contains iron, and the original experiments were made with this product. In view of the fact that cross standardisation was thus rendered impossible, Messrs. Peter Spence and Sons, Ltd., of Manchester, very kindly prepared and supplied me with some of the pure salt free from iron, so as to place the accuracy of the method beyond doubt.

In carrying out the titration, the usual necessary precautions in the use of the reagent must be observed, and the analyses must be made in cold solution. The solution must be preserved from the air unless check determinations are done with every batch of estimations.

Even this is less satisfactory than using a suitable apparatus, with a hydrogen generator attached (compare Knecht, "Journal of the Society of Dyers and Colourists," 1903, 19, 169, also Sutton's "Volumetric Analysis," 9th ed., 224). The special arrangement is, when once set up, more simple to use than an ordinary burette. Solutions of titanium trichloride of various strengths were used. The usual solution was made by boiling 50 cc. of the strong solution (commercial 20 per cent.) with 50 cc. of strong hydrochloric acid and diluting to two litres. Its strength corresponded approximately to 0·003 gram of copper per cc. The results obtained were as follow :—

Standardisation by Iron. Seven grams of ferrous ammonium sulphate were dissolved in water and made up to a litre (1 cc. = 0·001 gram Fe). The solution was oxidised with potassium permanganate run in from a burette.

(1) 50 cc. iron solution required 19·4 cc. titanium trichloride.
(2) ,, ,, ,, ,, 19·4 ,, ,, ,,
(3) ,, ,, ,, ,, 19·35 ,, ,, ,,

Mean................ 19·38

$$\text{Fe equivalent} = \frac{0·05}{19·38} = 0·00258 \text{ gram.}$$

Copper Solution. Recrystallised copper sulphate equal to 0·99765 gram of copper was weighed out and made up to a litre.

Potassium Thiocyanate Solution. One hundred grams of the salt were dissolved and made up to a litre. From 10 to 20 cc. were added to each titration.

(1) 50 cc. copper solution required 17·00 cc. titanium trichloride.
(2) ,, ,, ,, ,, 17·05 ,, ,, ,,
(3) ,, ,, ,, ,, 17·00 ,, ,, ,,

Fe value of solution = 0·00258.

$$\text{Cu value} = 0·00258 \times \frac{63·5}{56} = 0·00293.$$

Copper found = 0·00293 × 17·02 = 0·04986 gram, equal to 99·95 per cent. of the copper present in the pure salt.

The amounts of potassium thiocyanate, acid (either sulphuric or hydrochloric), and water used were varied in a large number of experiments, but no alteration in the quantity of titanium trichloride could be detected.

TITRATION IN PRESENCE OF FERRIC AND CUPRIC SALT.

Copper solution.	Iron alum solution.	H_2SO_4 (1 : 1)	$TiCl_3$ solution.*
20 cc.	—	10 cc.	10·5 cc.
—	20 cc.	10 ,,	12·05 ,,
20 ,,	20 ,,	10 ,,	22·5 ,,
20 ,,	20 ,,	10 ,,	22·5 ,,

* This was a weaker solution than that used in the foregoing experiments.

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Total copper and iron may therefore be estimated in the same solution. The presence of such salts as ammonium chloride, sodium acetate, zinc sulphate or chloride, ferrous sulphate, and stannic chloride exerts no influence on the course of the reaction.

Effect of Temperature. At 80° the reagent is decomposed with precipitation of titanium dioxide. At 40° the first addition of a few cc. discharged the red colour, but it quickly returned as the liquid cooled. Further additions were made and the amount finally required was the same as when cold, making a slight allowance for the oxidation resulting from longer exposure during titration.

$$\begin{aligned}\text{TiCl}_3 \text{ required in the cold} &\text{......................} && 10\cdot65 \text{ cc.}\\ \text{TiCl}_3 \text{ required at } 40° \text{ and cooling down} &\text{......} && 10\cdot72 \text{ cc.}\end{aligned}$$

Below 30° the amount required was not affected by variation in temperature.

Effect of Nitric Acid. Owing to its reduction by titanium trichloride, this acid must be absent.

Ferric Salts. Iron in the ferric state must be absent from the solution titrated, or the copper value of the amount of iron so present deducted from the result after it has been separately determined. The iron may be removed as acetate in the ordinary manner before titrating the copper. To test the method by comparison with others, a sample copper was analysed by the iodide, electrolytic, and the method here described, with the following results :—

Method.	Copper taken.	Copper found.	Percentage.
Electrolytic	0·25 gram	0·2498 gram	99·92
Titanium trichloride	0·25 ,,	0·2497 ,,	99·88
Iodide	0·25 ,,	0·2496 ,,	99·84

My thanks are due to Mr. G. H. Gray and Miss Eva Hibbert, who have assisted me with the analytical work.

PICRIC ACID ADDITIVE COMPOUNDS. F. S. SINNATT. ("Proceedings of the Chemical Society," 1905, 18, 297.) Knecht and Hibbert's process for the determination of picric acid has been found to be applicable to picric acid additive compounds. A number of additive compounds were prepared in a state of purity and examined.

DETERMINATION OF NITRATES. F. S. SINNATT. ("Proceedings of the Chemical Society," 1906, 22, 255). The process depends upon the conversion of the nitrate into picric acid by treatment with phenolsulphonic acid, and the subsequent determination of the picric acid formed by means of titanous chloride. The error is not so great as when the colorimetric process is used.

THE ESTIMATION OF NAPHTHALENE IN COAL GAS. F. S. SINNATT. ("Journal of Gas Lighting," vol. 93, p. 288.) The

naphthalene is separated as the picric acid additive compound from a measured volume of the gas. Any of the well-known processes may be used. The naphthalene picrate is dissolved in 20 cc. of absolute alcohol, and 20 cc. of hydrochloric acid added. The solution is now titrated with titanous chloride solution. The value of the titanous chloride solution in grams of naphthalene is known.

THE ABSORPTION OF OXYGEN BY SOLUTIONS OF SODIUM HYDROSULPHITE. F. S. SINNATT. ("Gas World," 1906). A solution of sodium hydrosulphite in water can be used with advantage for the absorption of oxygen from gaseous mixtures. The solution does not react with many of the commonly estimated gases, and may be substituted for the alkaline solution of pyrogallic acid. Although the action is slower than that of the pyrogallic acid solution, the absorption of oxygen is more complete. The reaction is not retarded by low temperatures, and the deterioration of the solution does not lead to the evolution of any gas.

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